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Supporting Information

Propyl benzenecarboxylate. oil; R_f 0.63 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1718 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (t, J = 7.4 Hz, 3H), 1.71 (st, J = 7.3 Hz, 2H), 4.21 (t, J = 6.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 8.00 (dd, J = 1.2, 8.2 Hz, 2H); ^{13}C NMR (CDCl_3) δ 10.38, 22.02, 66.34, 128.19, 129.41, 130.44, 132.67, 166.45; EIMS m/z 164 (M^+ , 2 %), 123, 105 (100 %), 77, 51, 43, 164 calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$.

Dipropyl benzene-1, 2-dicarboxylate. oil; R_f 0.52 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1728 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.94 (t, J = 7.4 Hz, 6H), 1.58-1.70 (m, 4H), 4.21 (t, J = 6.7 Hz, 4H), 7.37-7.42 (m, 2H), 7.57-7.62 (m, 2H); ^{13}C NMR (CDCl_3) δ 10.34, 21.82, 67.14, 128.74, 130.64, 132.24, 167.60; EIMS m/z 250 (M^+ , 1 %), 149 (100 %), 104, 76, 43, 250 calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$.

Dimethyl benzene-1,3-dicarboxylate. mp 63-65 °C; R_f 0.47 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1722 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 3.99 (s, 6H), 7.45 (t, J = 7.8 Hz, 1H), 8.16 (dd, J = 1.7, 7.8 Hz, 2H), 8.62 (s, 1H); ^{13}C NMR (CDCl_3) δ 52.25, 128.53, 130.48, 130.60, 133.68, 165.68.

Dipropyl benzene-1, 3-dicarboxylate. oil; R_f 0.61 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1724 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.96 (t, J = 7.4 Hz, 6H), 1.73 (st, J = 7.1 Hz, 4H), 4.23 (t, J = 6.7 Hz, 4H), 7.45 (t, J = 7.8 Hz, 1H), 8.14 (dd, J = 1.6, 7.8 Hz, 2H), 8.61 (s, 1H); ^{13}C NMR (CDCl_3) δ 10.36, 21.98, 66.73, 128.40, 130.49, 130.81, 133.52, 165.68; EIMS m/z 250 (M^+ , 1 %), 209, 191 (100 %), 167, 149, 121, 104, 76, 65, 41, 250 calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$.

S, S-dipropyl benzene-1, 3-dicarbothioate. oil; R_f 0.77 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1666 (S-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.98 (t, J = 7.3 Hz, 6H), 1.69 (st, J = 1.69 Hz, 4H), 3.03 (t, J = 7.2 Hz, 4H), 7.48 (t, J = 7.8 Hz, 1H), 8.09 (dd, J = 1.7, 7.8 Hz, 2H), 8.50

(s, 1H); ^{13}C NMR (CDCl_3) δ 13.36, 22.82, 31.07, 125.82, 128.89, 137.53, 131.31, 191.14; EIMS

m/z 282 (M^+ , 7 %), 207 (100 %), 165, 137, 104, 76, 41, 282 calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}_2$.

Dimethyl benzene-1, 4-dicarboxylate. mp 135-137 °C; R_f 0.52 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1718 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 3.91 (s, 6H), 8.06 (s, 4H); ^{13}C NMR (CDCl_3) δ 52.36, 129.48, 133.83, 166.21; EIMS m/z 194 (M^+ , 22 %), 163 (100 %), 135, 120, 104, 76, 50, 40, 194 calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4$.

Dipropyl benzene-1, 4-dicarboxylate. oil; R_f 0.65 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1718 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.89 (t, J = 7.4 Hz, 6H), 1.64 (st, J = 7.1 Hz, 4H), 4.16 (t, J = 6.6 Hz, 4H), 7.96 (s, 4H); ^{13}C NMR (CDCl_3) δ 10.28, 21.89, 66.68, 129.26, 134.00, 165.53; EIMS m/z 250 (M^+ , 4 %), 209, 191 (100 %), 167, 149, 121, 104, 76, 65, 41, 250 calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$.

S, S-dipropyl benzene-1, 4-dicarbothioate. mp ca. 15-20 °C R_f 0.68 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1664 (S-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (t, J = 7.3 Hz, 6H), 1.69 (st, J = 7.2 Hz, 4H), 3.05 (t, J = 7.4 Hz, 4H), 8.00 (s, 4H); ^{13}C NMR (CDCl_3) δ 13.39, 22.80, 31.15, 127.30, 140.55, 191.38; EIMS m/z 282 (M^+ , 7 %), 207 (100 %), 179, 137, 104, 76, 41, 282 calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}_2$.

Hexamethyl benzenehexacarboxylate. mp 186-188 °C; R_f 0.06 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1740 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 5.22 (s); ^{13}C NMR (CDCl_3) δ 53.46, 133.86, 165.09.

Propyl pyridine-2-carboxylate. oil; R_f 0.12 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1718, 1740 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.84 (t, J = 7.4 Hz, 3H), 1.67 (st, J = 7.3 Hz, 2H), 4.20 (t, J = 6.9 Hz, 2H), 7.30 (ddd, J = 1.1, 4.8, 7.5 Hz, 1H), 7.67 (dt, J = 1.7, 7.7 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 8.58 (dd, J = 0.7, 4.0 Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.19, 21.85, 67.22,

124.90, 126.66, 136.85, 148.02, 149.66, 165.00; EIMS *m/z* 165 (M^+ , 1 %), 106, 93, 79 (100 %), 51, 39, 165 calcd for $C_9H_{11}NO_2$.

Propyl pyridine-3-carboxylate. oil; R_f 0.24 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1721 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.81 (t, J = 7.4 Hz, 3H), 1.59 (st, J = 7.0 Hz, 2H), 4.10 (t, J = 6.6 Hz, 2H), 7.18 (dd, J = 4.9, 7.9 Hz, 1H), 8.08 (dt, J = 1.5, 7.9 Hz, 1H), 8.55 (dd, J = 1.4, 4.8 Hz, 1H), 9.01 (s, 1H); ^{13}C NMR (CDCl_3) δ 10.20, 21.79, 66.69, 123.07, 126.12, 136.79, 150.53, 153.00, 164.97; EIMS *m/z* 165 (M^+ , 5 %), 164, 124, 106 (100 %), 78, 51, 41, 165 calcd for $C_9H_{11}NO_2$.

Propyl pyridine-4-carboxylate. oil; R_f 0.25 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1731 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, J = 7.4 Hz, 3H), 1.64 (st, J = 7.2 Hz, 2H), 4.15 (t, J = 6.7 Hz, 2H), 7.69 (dd, J = 1.5, 4.5 Hz, 2H), 8.61 (dd, J = 1.4, 4.5 Hz, 2H); ^{13}C NMR (CDCl_3) δ 10.24, 21.79, 67.10, 122.66, 137.47, 150.34, 164.88; EIMS *m/z* 165 (M^+ , 9 %), 164, 124, 106 (100 %), 78, 51, 41, 165 calcd for $C_9H_{11}NO_2$.

Dipropyl pyridine-2, 3-dicarboxylate. oil; R_f 0.22 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1729 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.86-0.93 (m, 6H), 1.57-1.65 (m, 4H), 4.17 (t, J = 6.7 Hz, 3H), 4.24 (t, J = 6.9 Hz, 4H), 7.38 (dd, J = 4.8, 7.9 Hz, 1H), 8.09 (dd, J = 1.7, 7.9 Hz, 1H), 8.64 (dd, J = 1.6, 4.8 Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.24, 21.71, 21.88, 67.49, 67.64, 124.58, 126.06, 137.53, 151.25, 151.62, 165.09, 166.34; EIMS *m/z* 251 (M^+ , 1 %), 179, 164, 150 (100 %), 124, 106, 79, 41, 251 calcd for $C_{13}H_{17}NO_4$.

Dipropyl pyridine-2, 4-dicarboxylate. oil; R_f 0.20 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1732 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H), 1.60-1.76 (m, 4H), 4.18 (t, J = 6.7 Hz, 2H), 4.24 (t, J = 6.8 Hz, 2H), 7.87 (dd, J = 1.5, 5.0 Hz, 1H), 8.45 (d, J = 0.7 Hz, 1H), 8.75 (d, J = 4.9 Hz, 1H); ^{13}C NMR (CDCl_3) δ 10.19, 21.76, 21.82,

67.5, 124.05, 125.75, 138.86, 149.10, 150.53, 164.13, 164.38; EIMS *m/z* 251 (M^+ , 2 %), 192, 179, 165 (100 %), 123, 77, 41, 251 calcd for $C_{13}H_{17}NO_4$.

Dimethyl pyridine-2, 5-dicarboxylate. mp 156-159 °C; R_f 0.14 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1721 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 3.90 (s, 3H), 3.95 (s, 3H), 8.13 (d, J = 8.1 Hz, 1H), 8.37 (dd, J = 2.1, 8.2 Hz, 1H), 9.21 (d, J = 1.5 Hz, 1H); ^{13}C NMR (CDCl_3) δ 52.67, 53.11, 124.59, 128.51, 138.25, 150.60, 164.70, 164.74; EIMS *m/z* 195 (M^+ , 2 %), 165, 137 (100 %), 77, 59, 195 calcd for $C_9H_9NO_4$.

Dipropyl pyridine-2, 5-dicarboxylate. oil; R_f 0.40 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1725 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.83 (t, J = 7.4 Hz, 6H), 1.59-1.74 (m, 4H), 4.17 (t, J = 6.6 Hz, 2H), 4.22 (t, J = 6.9 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H), 8.27 (dd, J = 2.0, 8.2 Hz, 1H), 9.15 (s, 1H); ^{13}C NMR (CDCl_3) δ 10.19, 21.80, 67.14, 67.59, 124.38, 128.55, 137.96, 150.57, 150.92, 164.23; EIMS *m/z* 251 (M^+ , 1 %), 179, 165 (B), 123, 105, 77, 41, 251 calcd for $C_{13}H_{17}NO_4$.

S, S-dipropyl pyridine-2, 5-dicarbothioate. oil; R_f 0.72 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1661 (S-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.90 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H), 1.58 (st, J = 7.3 Hz, 2H), 1.59 (st, J = 7.3 Hz, 3H), 2.90 (t, J = 7.4 Hz, 2H), 2.97 (t, J = 7.4 Hz, 2H), 7.89 (dd, J = 0.6, 8.4 Hz, 1H), 8.21 (dd, J = 2.2, 8.1 Hz, 1H), 9.1 (d, J = 1.6 Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.27, 13.39, 22.52, 22.63, 30.67, 31.10, 119.93, 135.83, 147.61, 135.32, 154.33, 189.54, 192.50; EIMS *m/z* 283 (M^+ , 6 %), 255, 213, 200, 181 (100 %), 138, 105, 77, 43, 283 calcd for $C_{13}H_{17}NO_2S_2$.

Dimethyl pyridine-2, 6-dicarboxylate. mp 118-120 °C; R_f 0.07 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1744 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 3.93 (s, 6H), 7.96 (t, J = 7.6 Hz, 1H), 8.23 (d, J = 7.6 Hz, 2H); ^{13}C NMR (CDCl_3) δ 53.08, 127.95, 138.34, 148.08, 164.93; EIMS *m/z* 195 (M^+ , 2 %), 165, 137 (100 %), 105, 77, 59, 195 calcd for $C_9H_9NO_4$.

Dipropyl pyridine-2, 6 dicarboxylate. oil; R_f 0.32 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1721, 1745 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.86 (t, J = 7.4 Hz, 6H), 1.68 (st, J = 7.3 Hz, 4H), 4.20 (t, J = 6.9 Hz, 4H), 7.88 (t, J = 8.0 Hz, 1H), 8.10 (d, J = 7.7 Hz, 2H); ^{13}C NMR (CDCl_3) δ 10.15, 27.76, 67.41, 127.55, 138.13, 148.44, 164.38; EIMS m/z 251 (M^+ , 2 %), 179, 165 (B), 123, 105, 77, 41, 251 calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$.

S, S-dipropyl pyridine-2, 6-dicarbothioate. mp 47-48 °C; R_f 0.68 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1667 (S-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.02 (t, J = 7.2 Hz, 6H), 1.70 (st, J = 7.1 Hz, 4H), 3.00 (t, J = 7.2 Hz, 4H), 7.97 (t, J = 6.7 Hz, 1H), 8.09 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.57, 22.72, 30.66, 123.62, 138.59, 151.15, 192.90; EIMS m/z 283 (M^+ , 4 %), 255, 181 (100 %), 110, 105, 78, 283 calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{S}_2$.

Dipropyl pyridine-3, 4-dicarboxylate. oil; R_f 0.24 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1729 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.78-0.84 (m, 6H), 1.52-1.65 (m, 4H), 4.12 (t, J = 6.6 Hz, 4H) 7.34 (d, J = 4.8 Hz, 1H), 8.64 (d, J = 4.9 Hz, 1H), 8.88 (s, 1H); ^{13}C NMR (CDCl_3) δ 10.21, 21.64, 21.72, 67.45, 67.72, 121.69, 125.26, 140.46, 150.25, 152.59, 165.04, 166.19; EIMS m/z 251 (M^+ , 1 %), 210, 192, 150 (100 %), 123, 105, 77, 41, 251 calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$.

Dipropyl pyridine-3, 5-dicarboxylate. mp 58-61 °C; R_f 0.40 [ether-petroleum spirits (60-90 °C) 1 : 1]; IR (KBr) 1726 (O-C=O) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.02 (t, J = 7.4 Hz, 6H), 1.80 (st, J = 7.1 Hz, 4H), 4.32 (t, J = 6.7 Hz, 4H), 8.84 (t, J = 2.0 Hz, 1H), 9.34 (d, J = 2.0 Hz, 2H); ^{13}C NMR (CDCl_3) δ 10.37, 21.95, 67.40, 126.49, 138.31, 153.52, 164.28; EIMS m/z 251 (M^+ , 9 %), 210, 192, 168 (100 %), 150, 122, 105, 94, 77, 41, 251 calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$.

¹³C NMR supporting information which was used to identify compounds **3b** and **3c**. The ¹³C NMR spectra in the aromatic region for compounds **3b** and **3c** is sufficiently different to enable them to be identified.

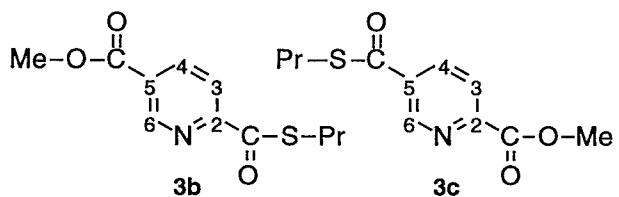
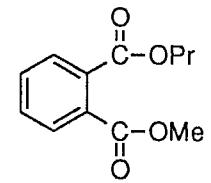


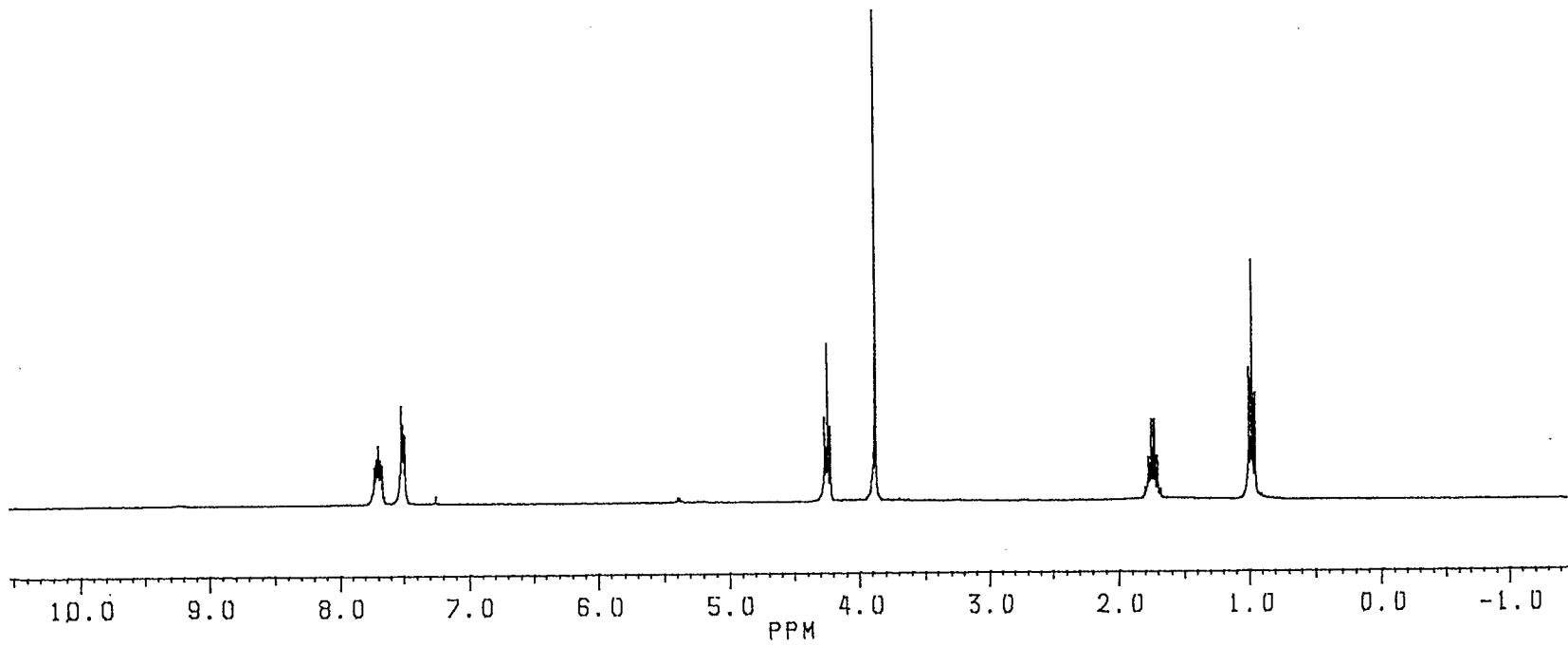
Table S1 gives the NMR data and shows that for compound **3b**, C2 and C3 have similar chemical shifts to the (S) ester (*S, S*-dipropyl pyridine-2, 5-dicarbothioate) and C5 and C6 have similar chemical shifts to the (O) ester (dipropyl pyridine-2, 5-dicarboxylate). The reverse applies for compound **3c**.

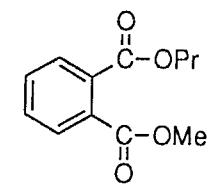
Compound	C=S	C=O	C2	C3	C4	C5	C6
dipropyl pyridine-2, 5-dicarboxylate		164.23	150.92	124.38	137.96	128.55	150.57
<i>S, S</i> -dipropyl pyridine-2, 5-dicarbothioate	192.50 189.54		154.33	119.93	135.73	135.32	147.61
methyl-2-(propylsulfanyl)-carbonylpyridine-5-carboxylate (4b)	192.88	164.79	154.45	119.77	138.44	129.13	150.16
methyl-5-(propylsulfanyl)-carbonylpyridine-2-carboxylate (4c)	189.86	164.74	150.79	124.87	135.60	134.85	148.22

Table S1. ¹³C NMR data for aromatic carbon atoms recorded in CDCl₃ at 25 °C. Data is in ppm and referenced to the solvent.

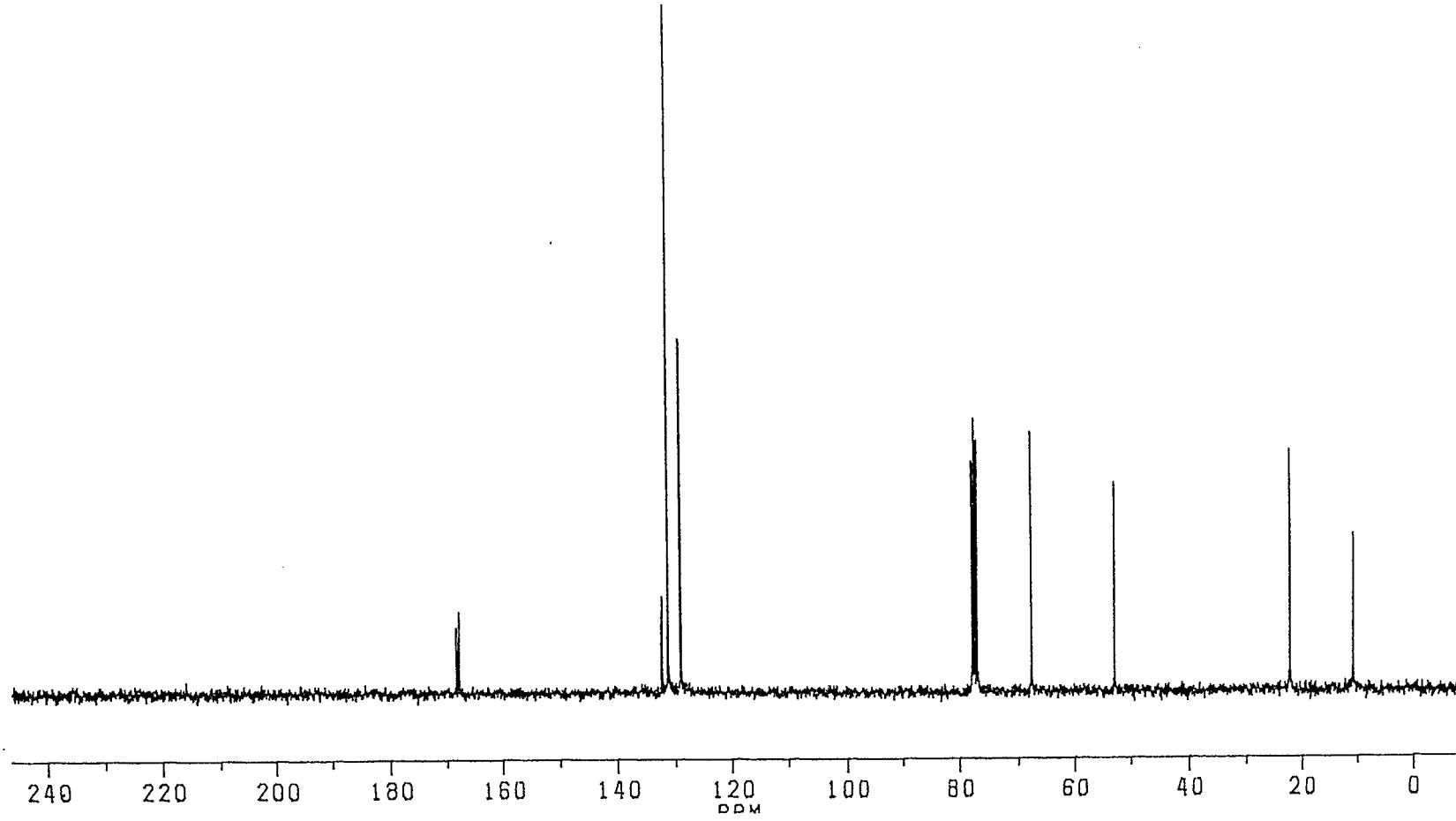


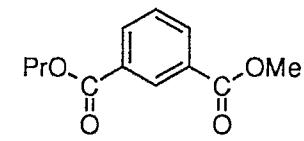
^1H NMR; 300 MHz; CDCl_3 ; 298 K



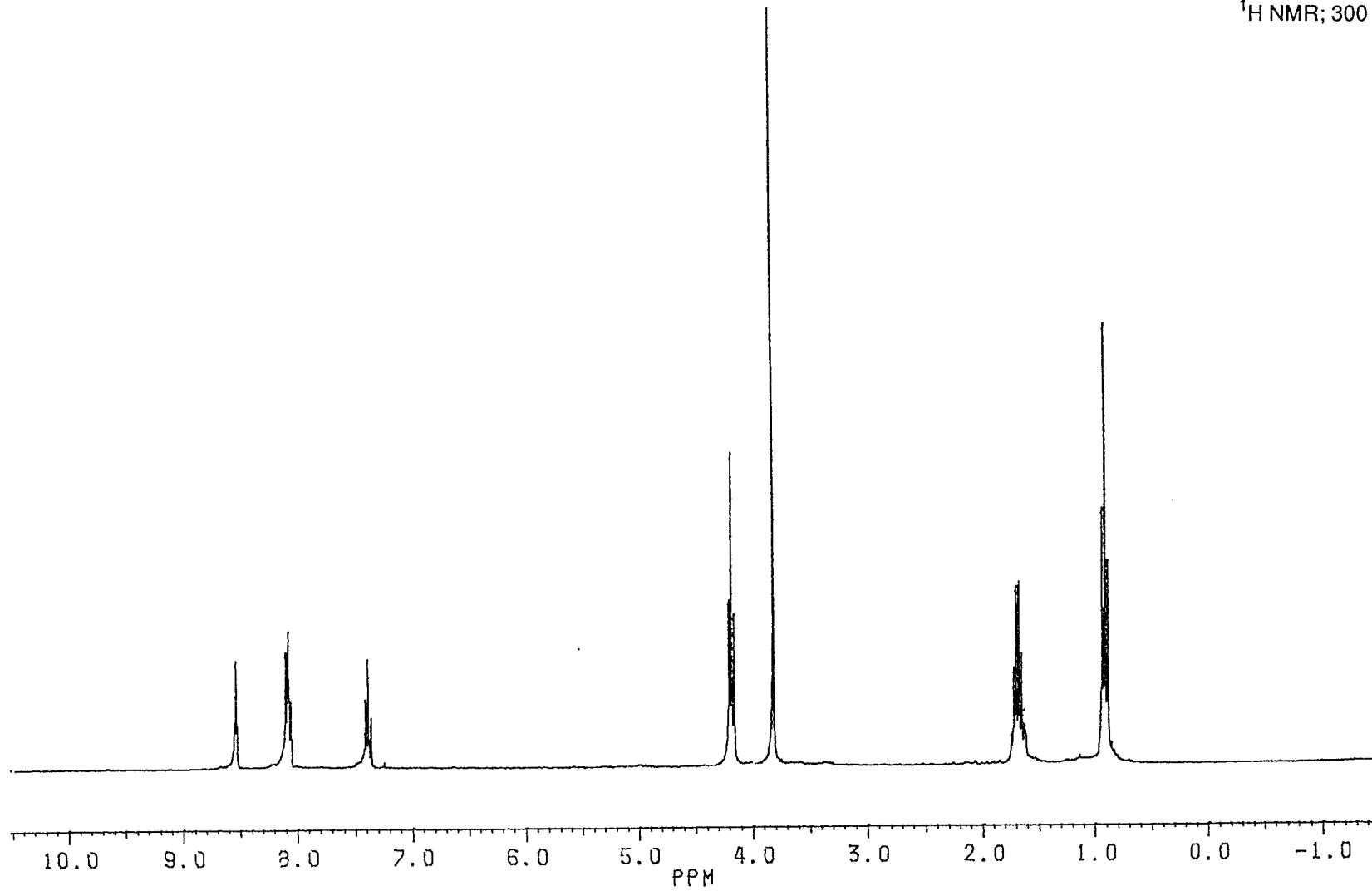


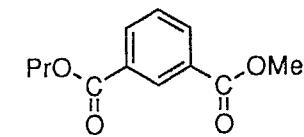
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



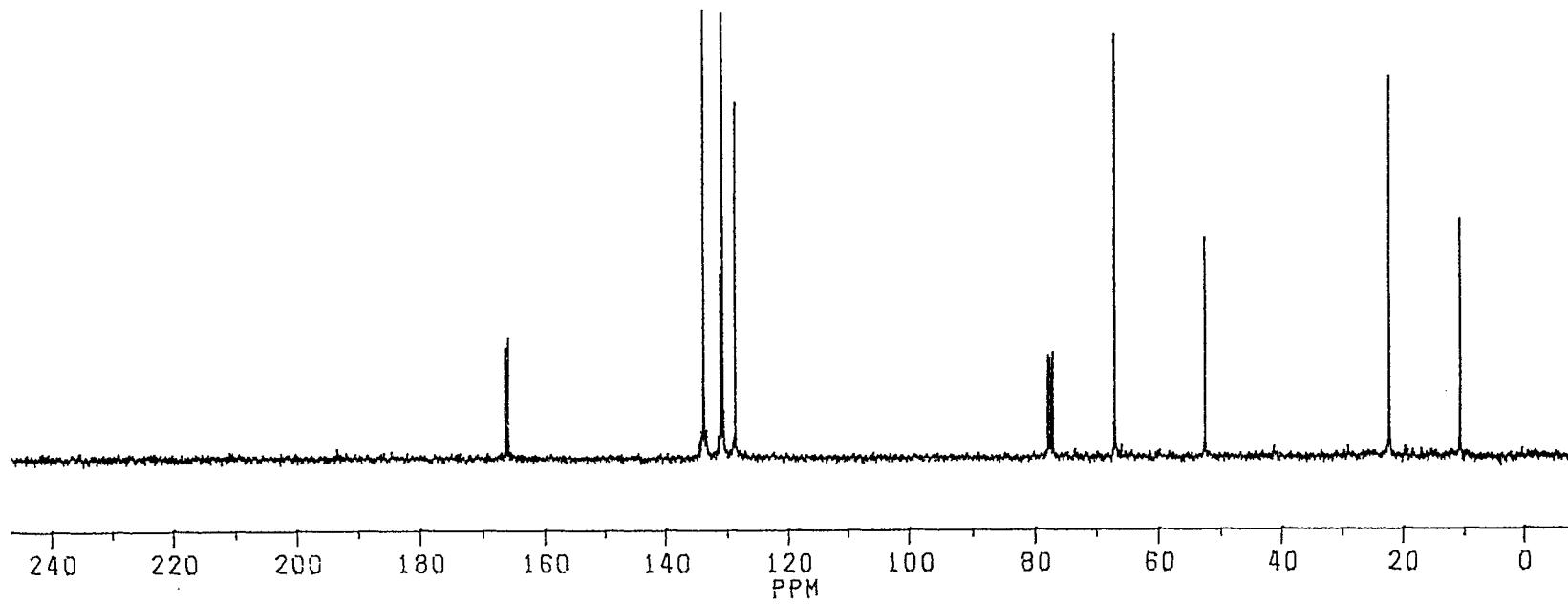


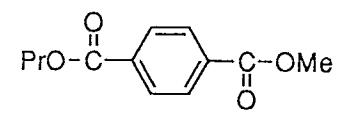
^1H NMR; 300 MHz; CDCl_3 ; 298 K



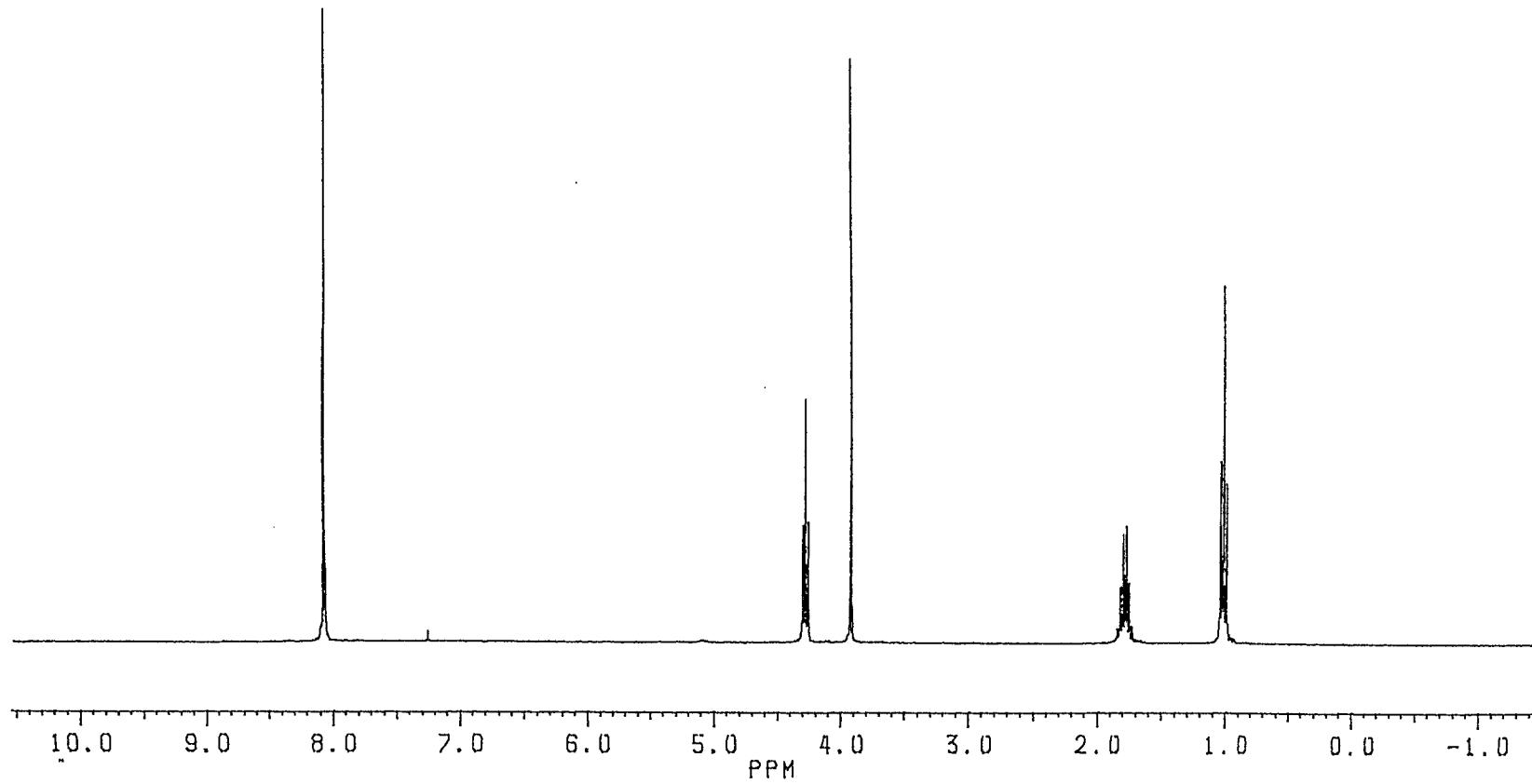


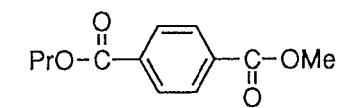
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



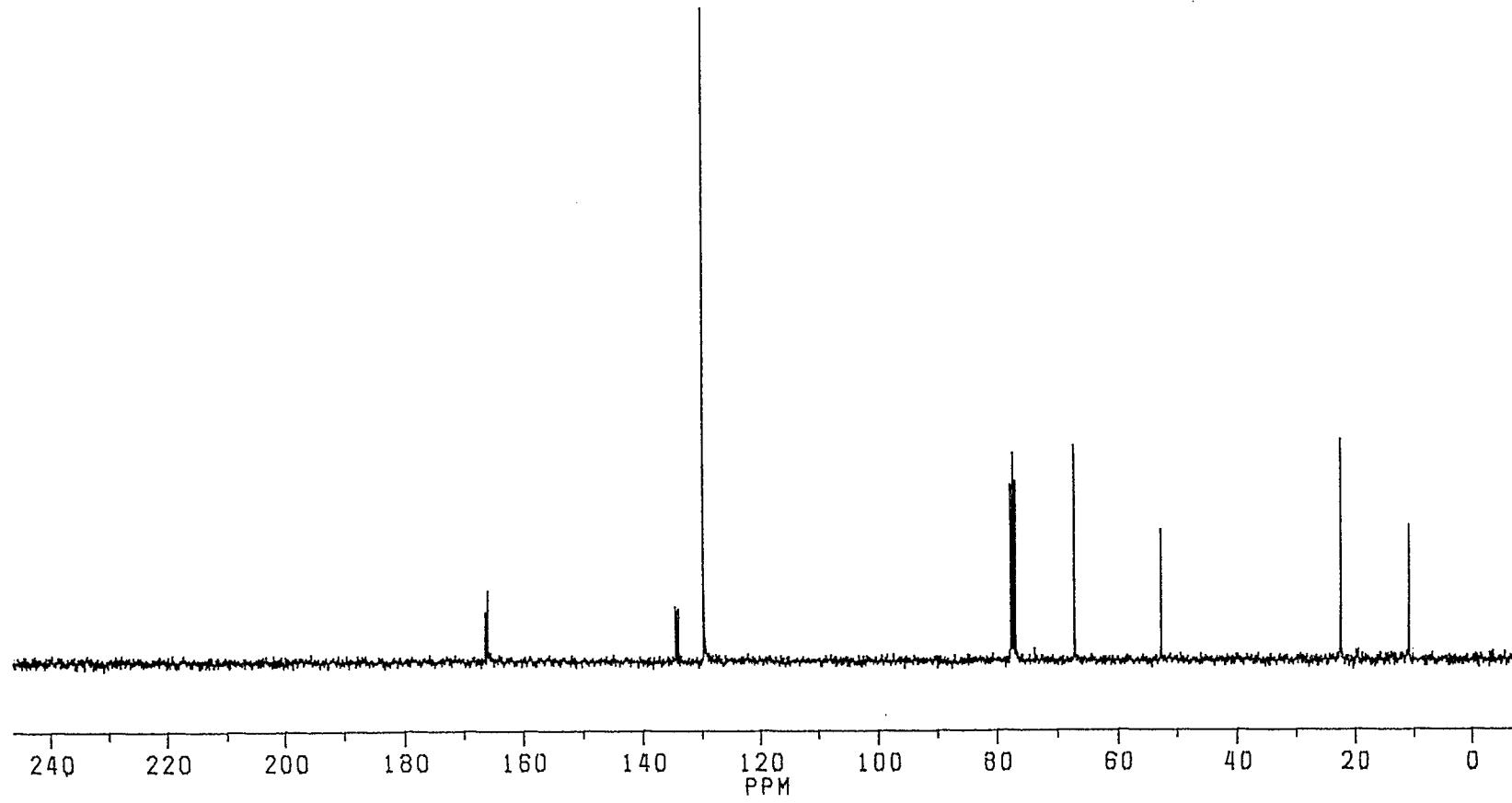


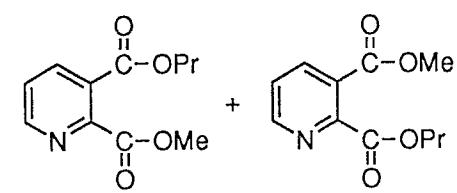
^1H NMR; 300 MHz; CDCl_3 ; 298 K



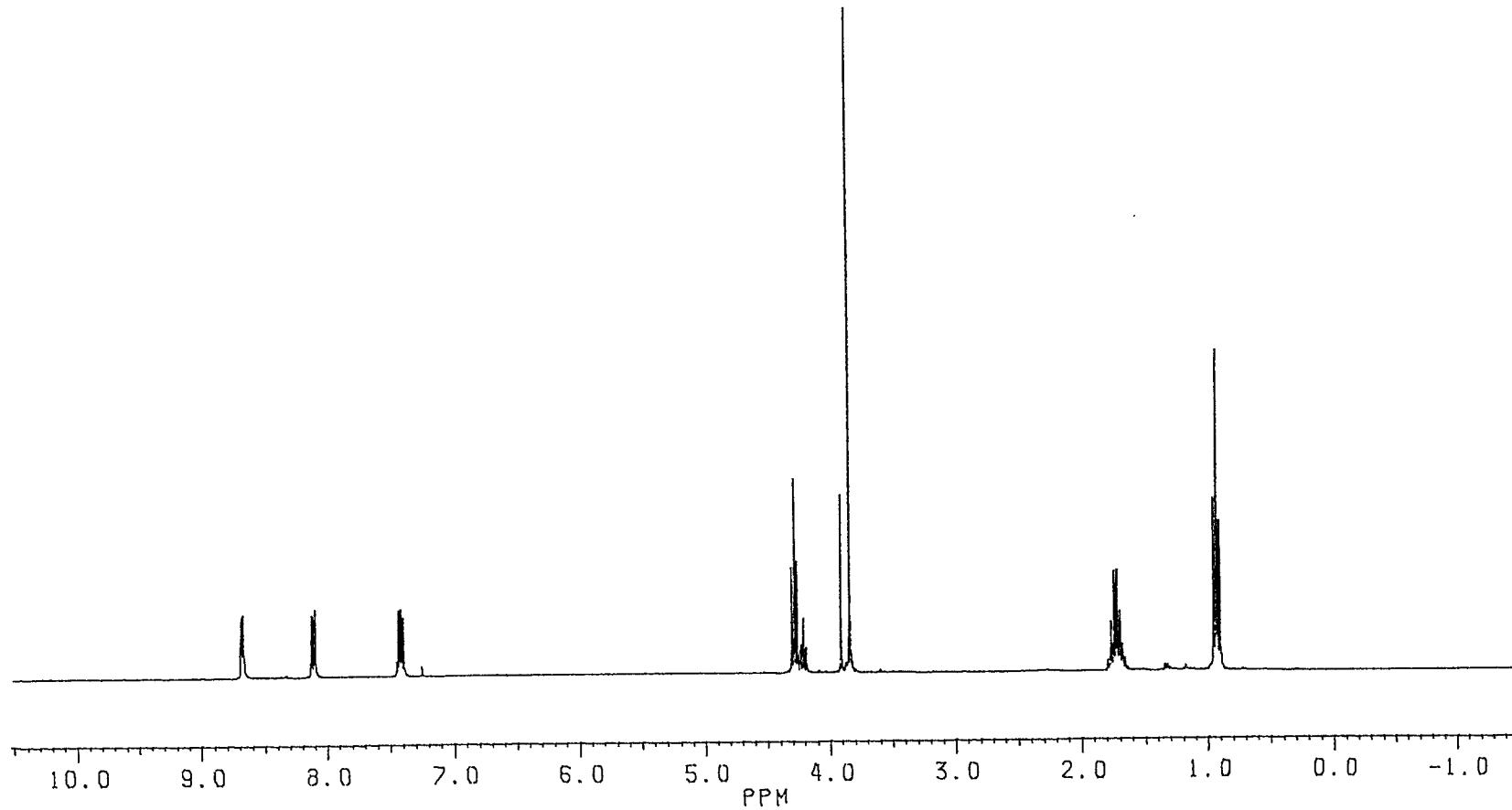


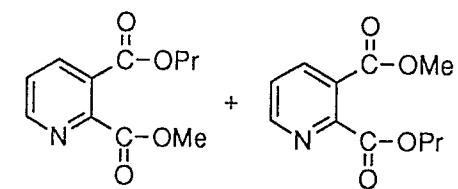
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



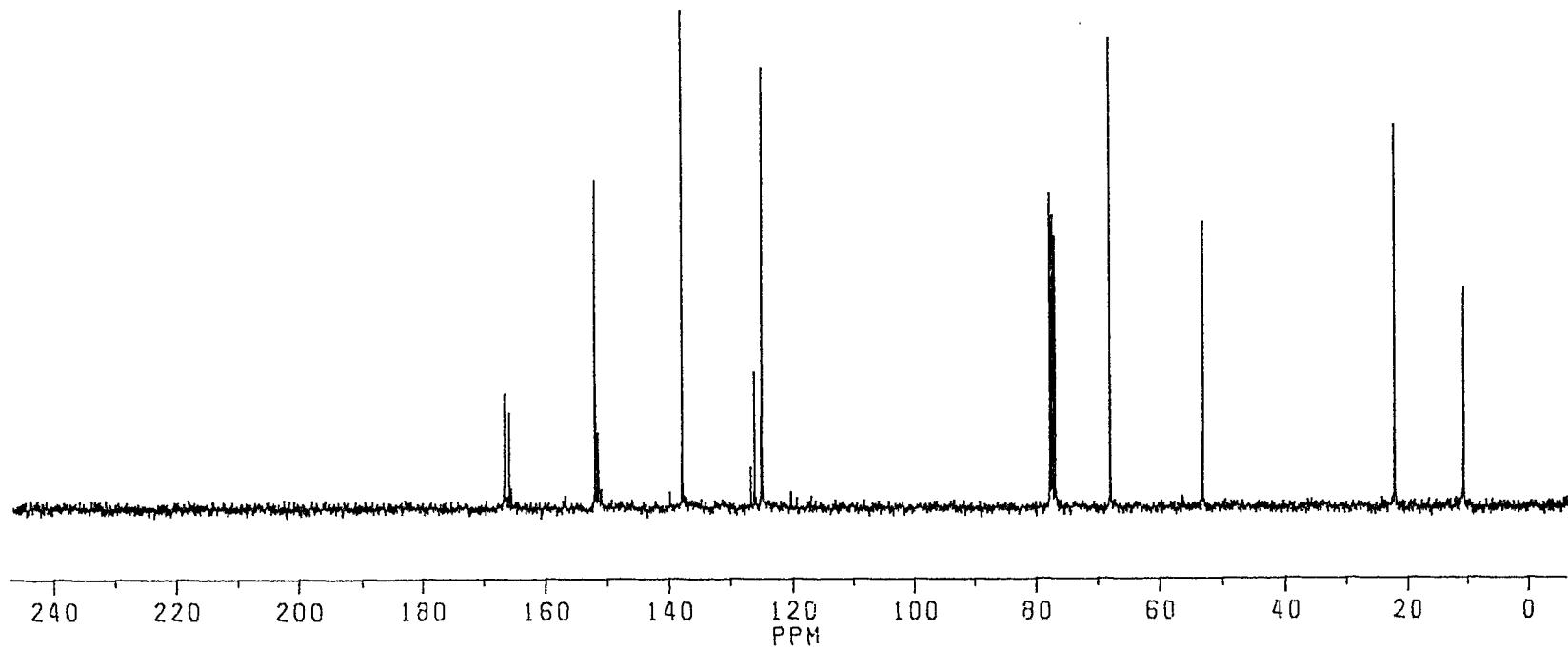


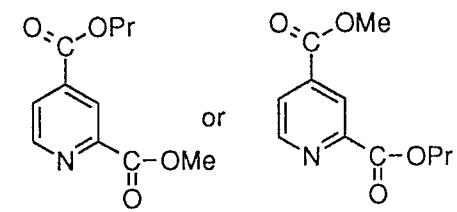
^1H NMR; 300 MHz; CDCl_3 ; 298 K



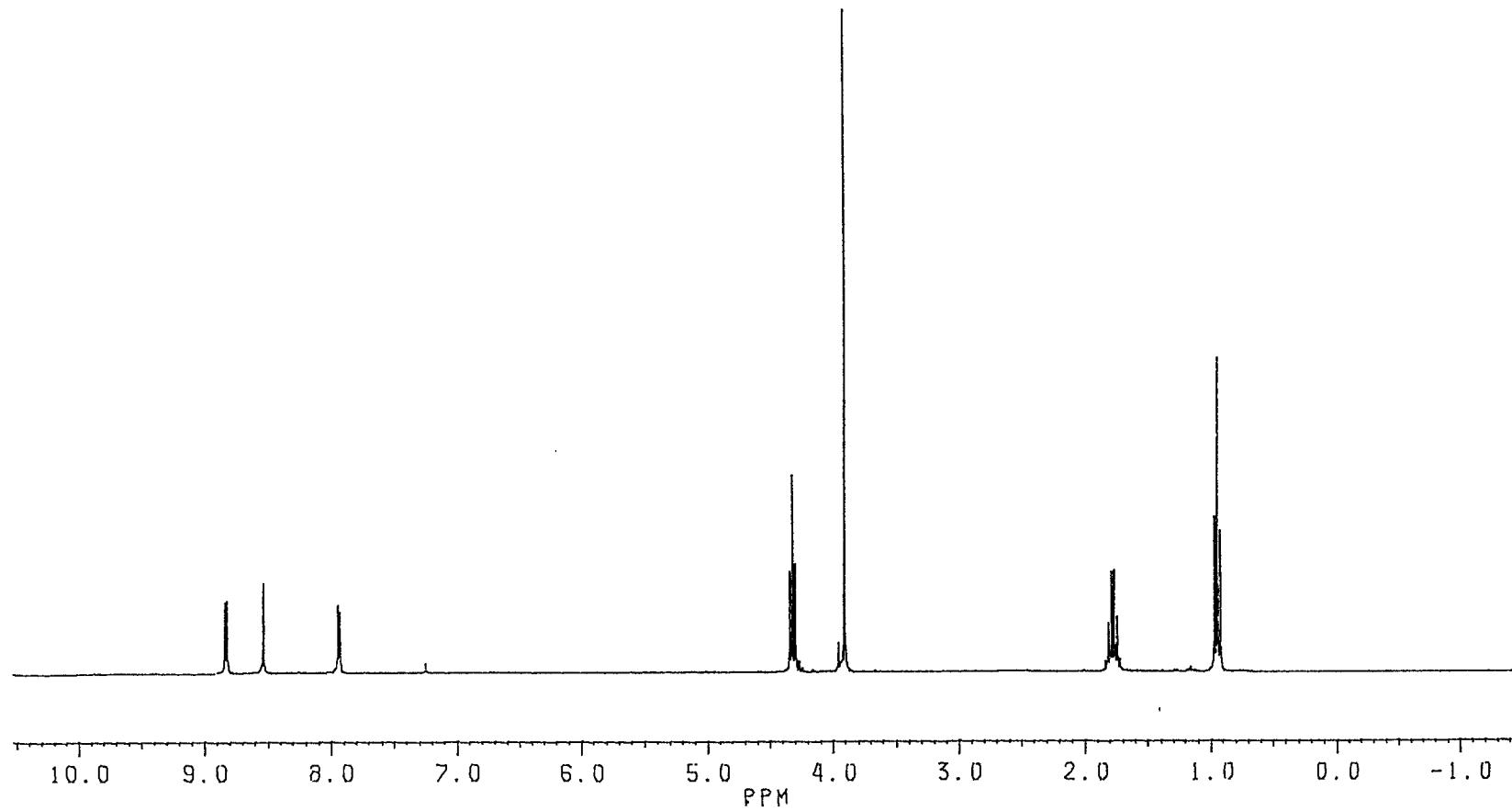


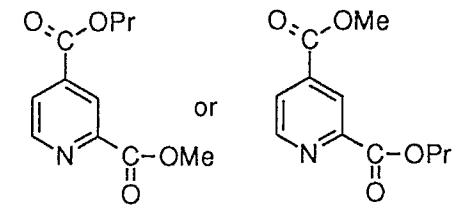
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



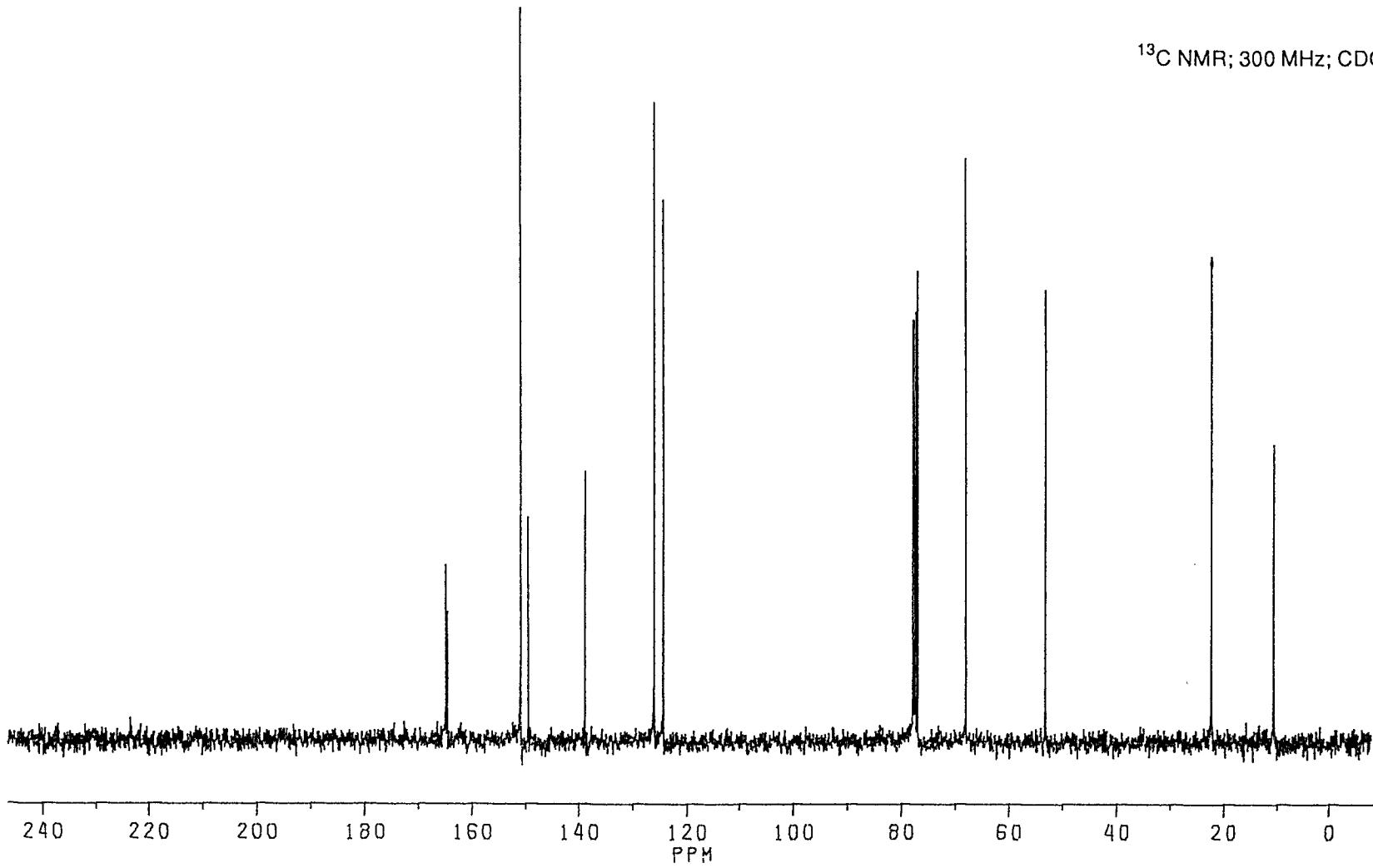


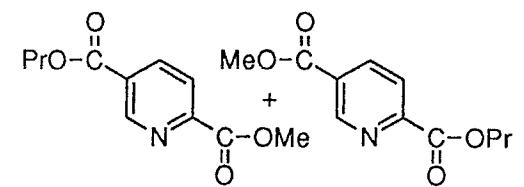
^1H NMR; 300 MHz; CDCl_3 ; 298 K



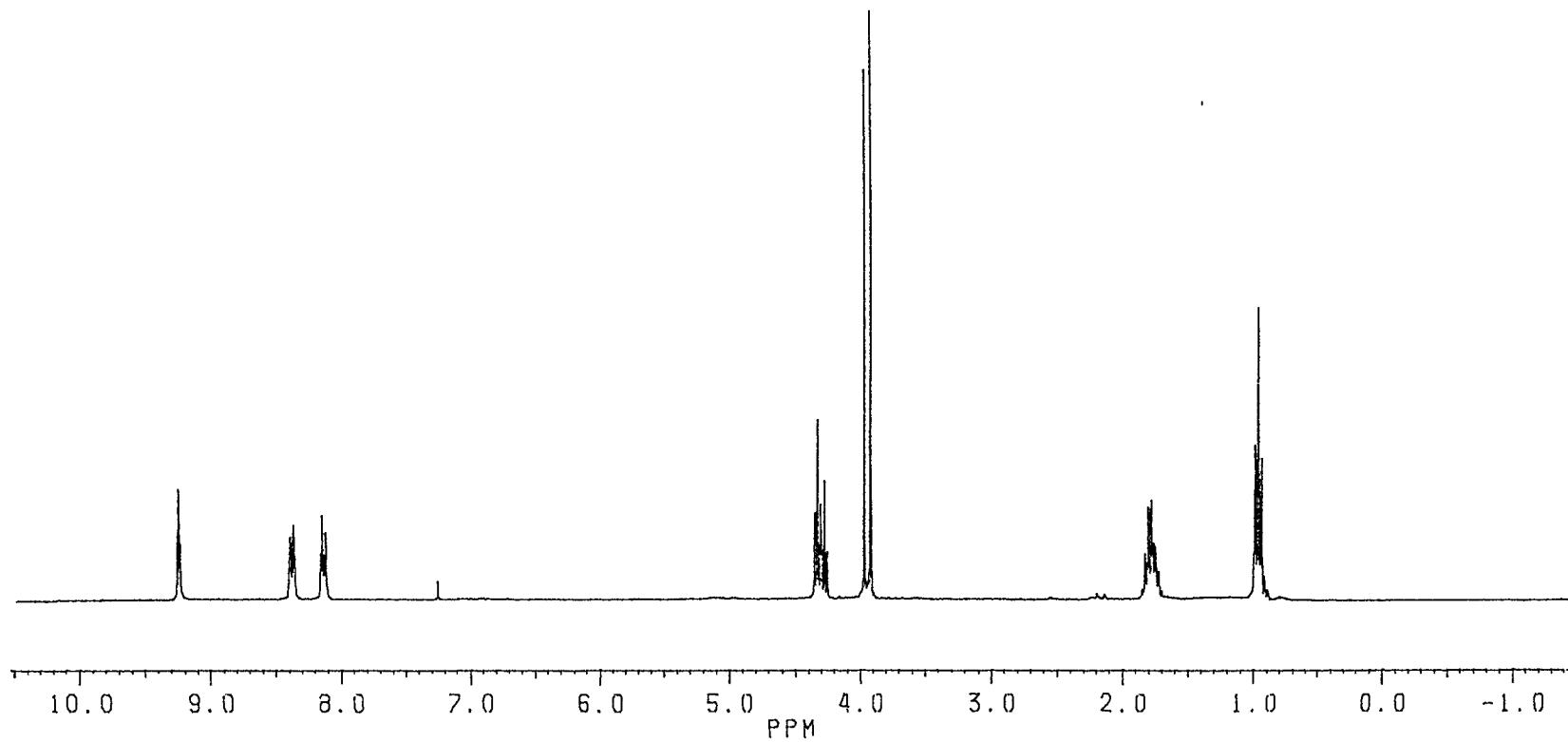


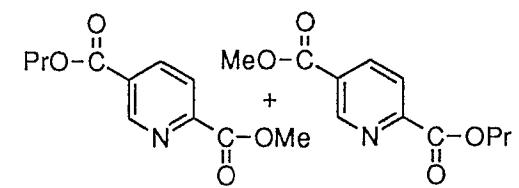
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



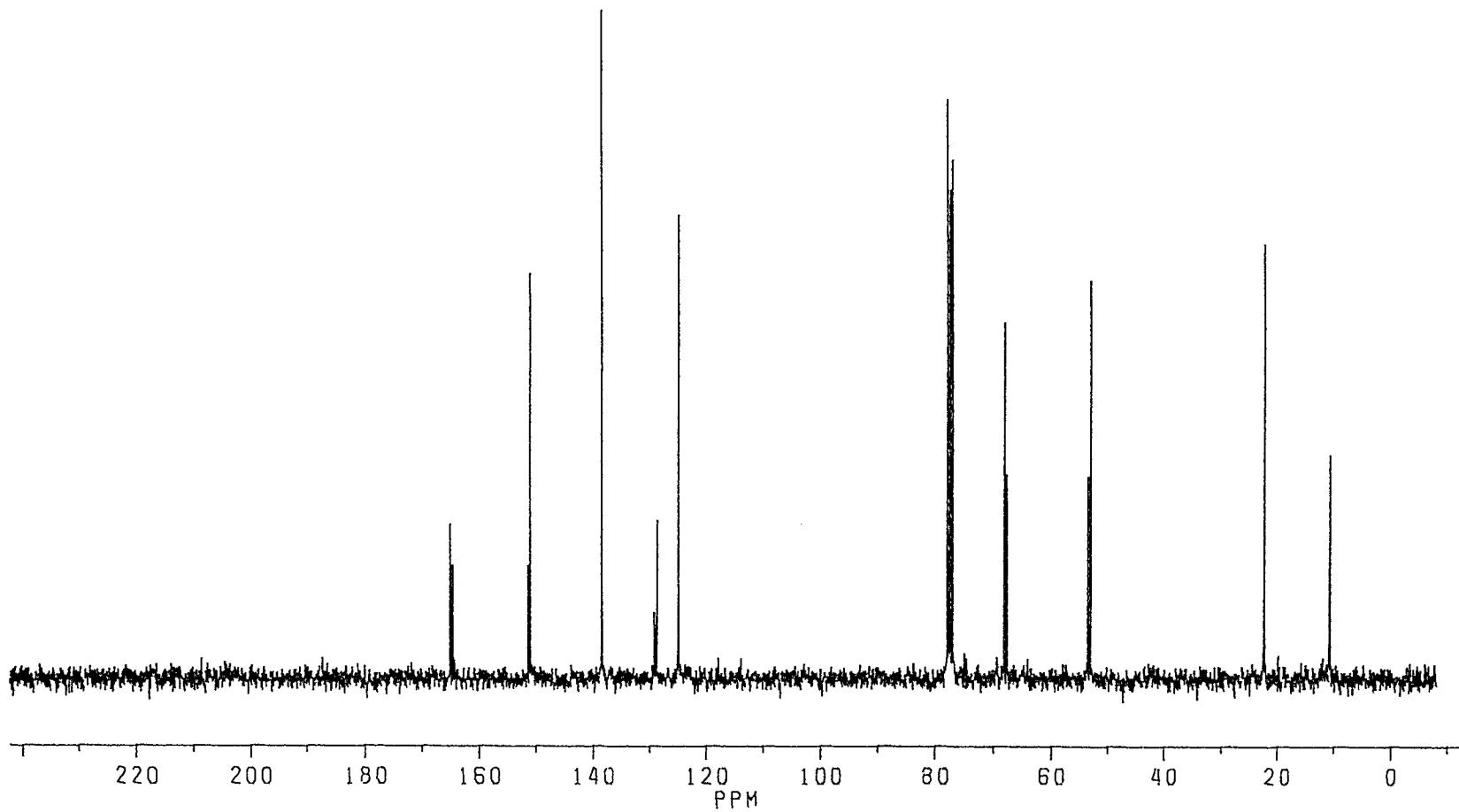


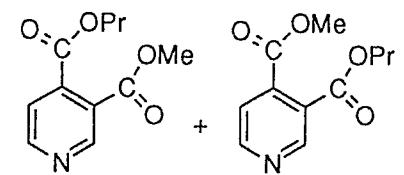
^1H NMR; 300 MHz; CDCl_3 ; 298 K



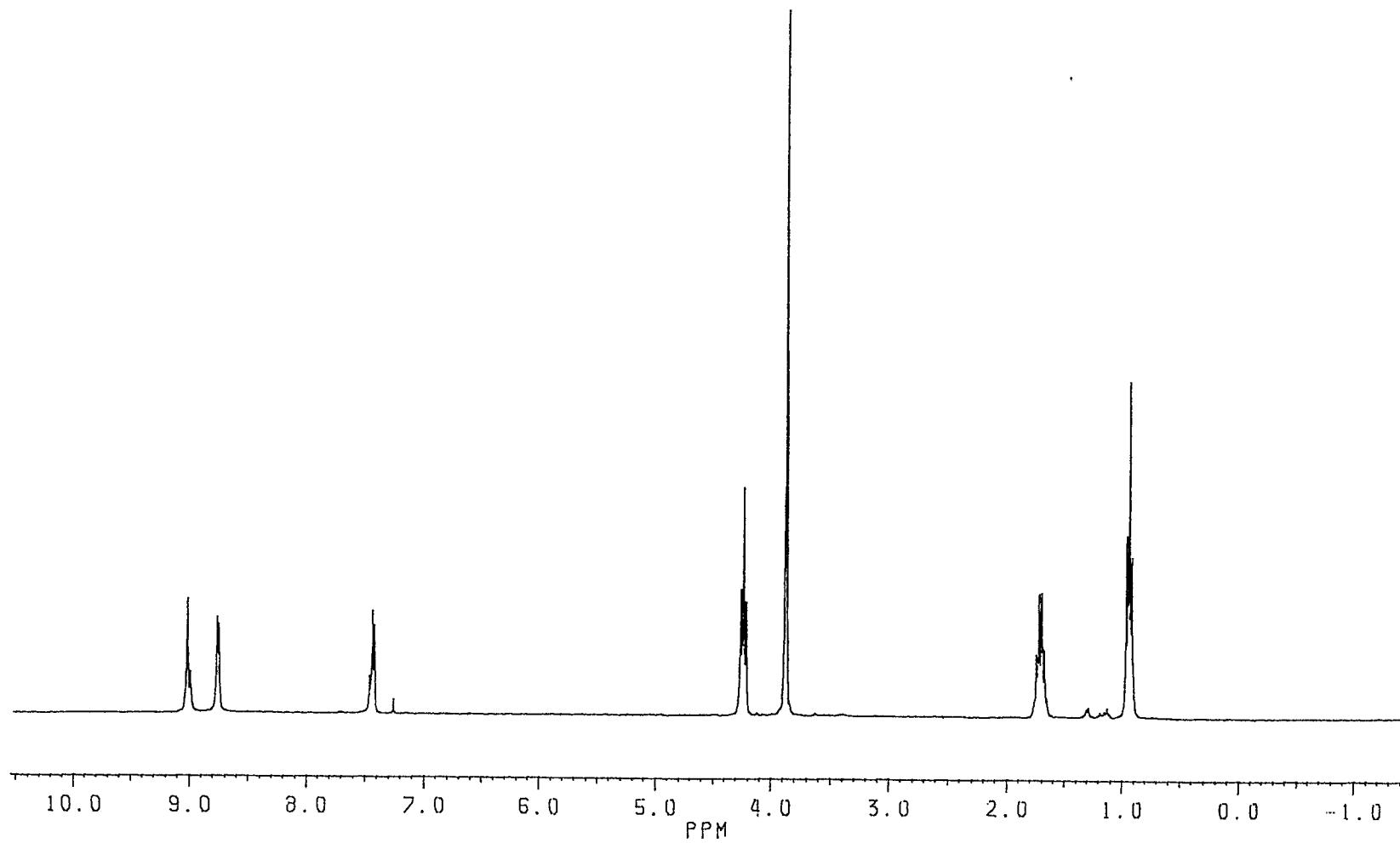


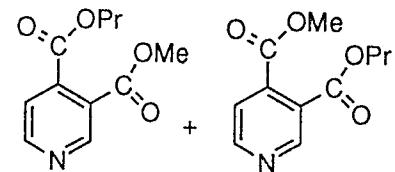
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



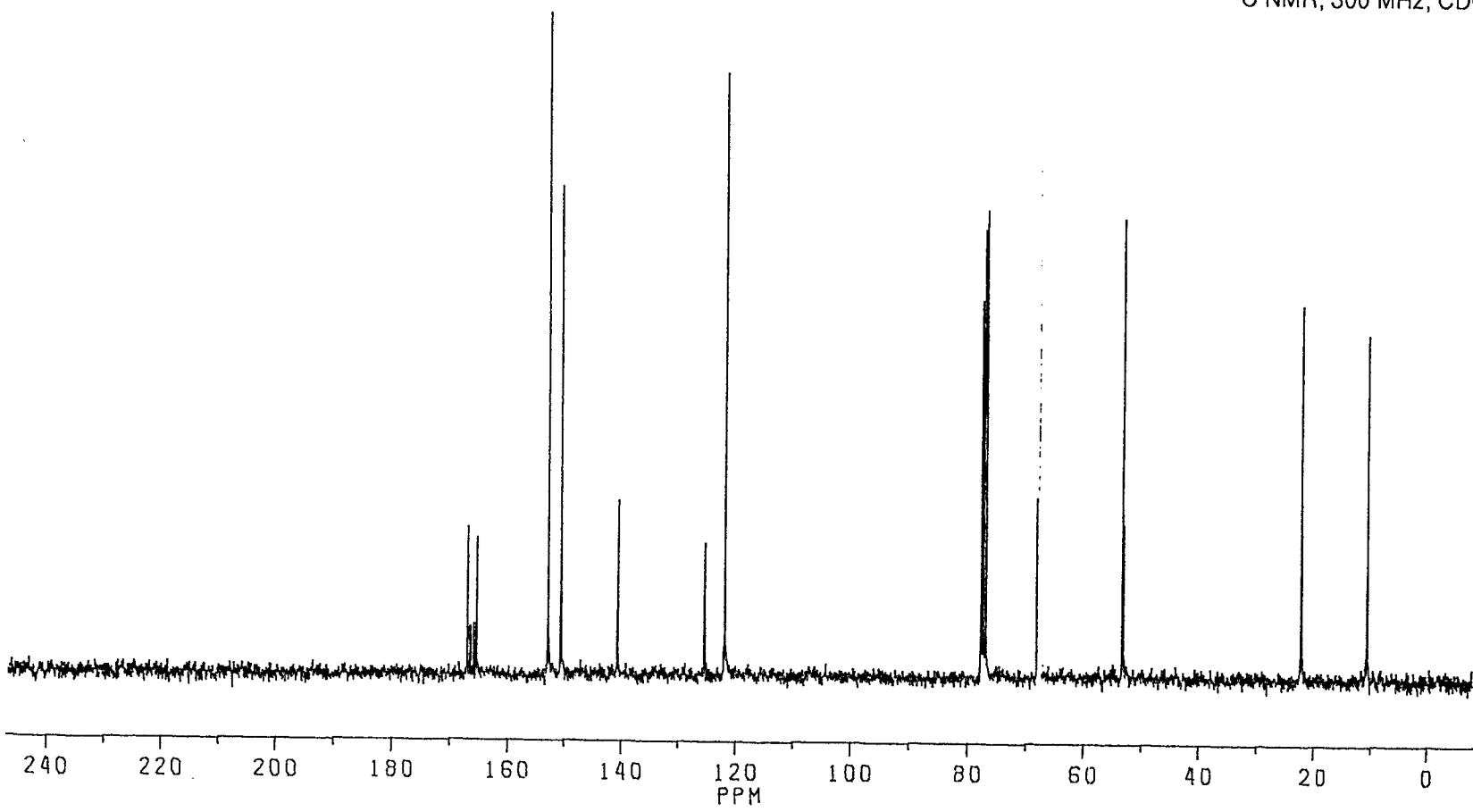


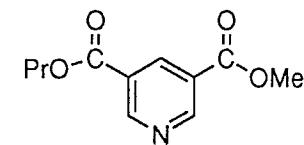
^1H NMR; 300 MHz; CDCl_3 ; 298 K



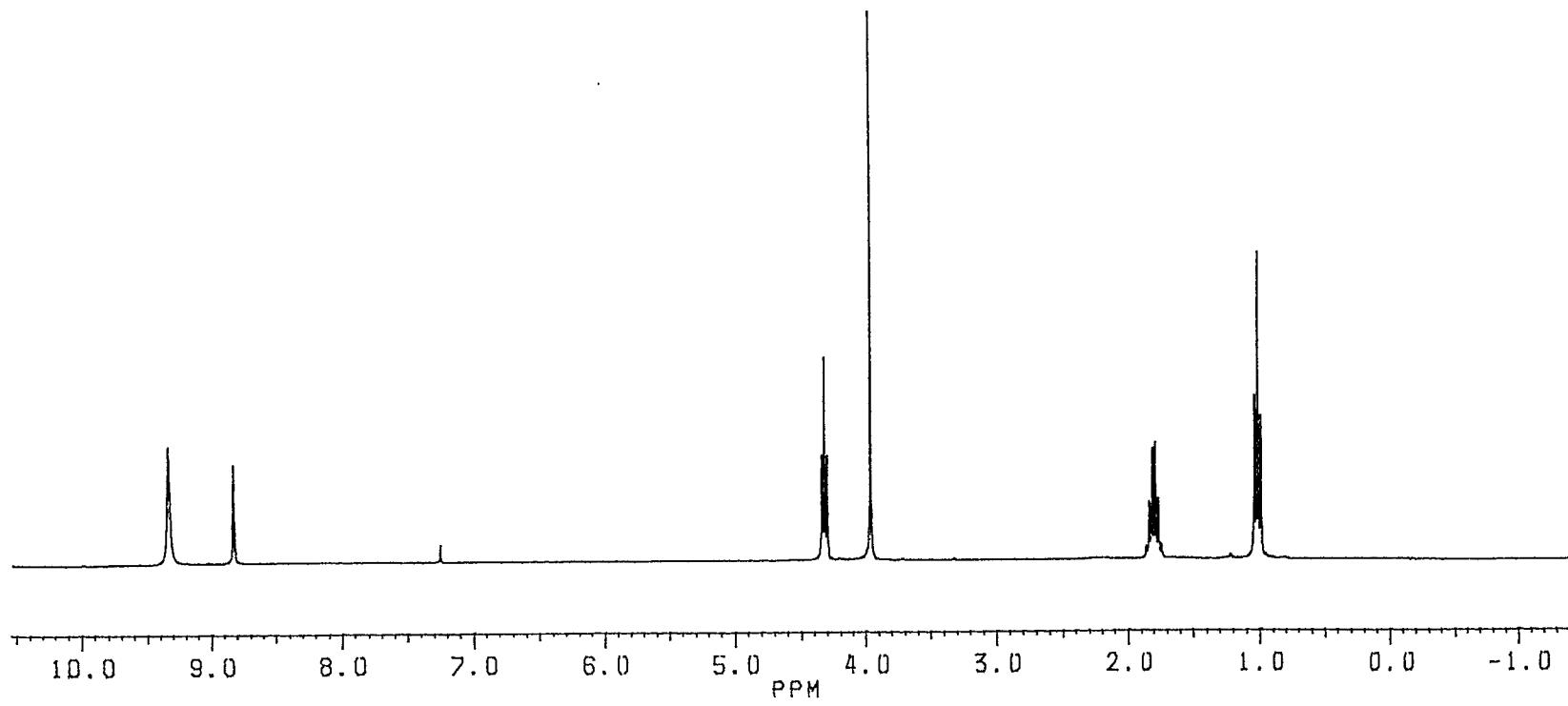


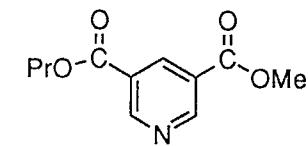
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



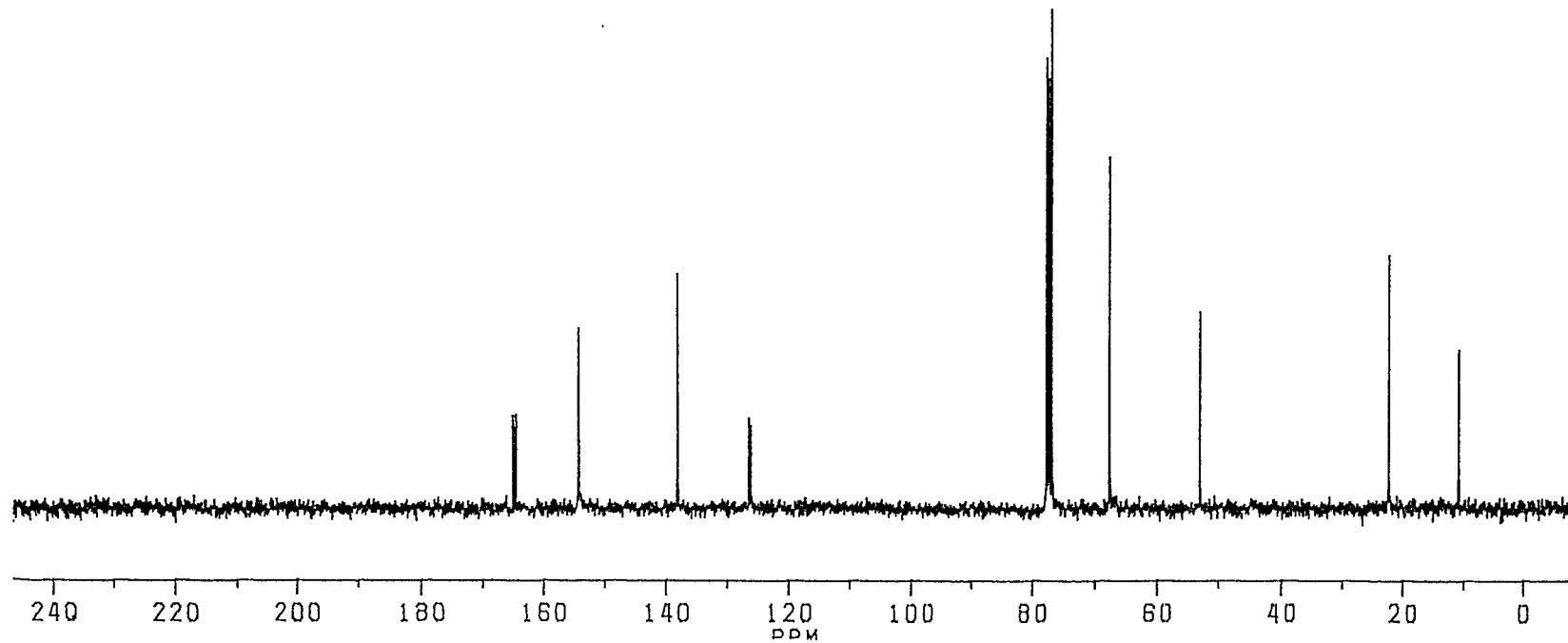


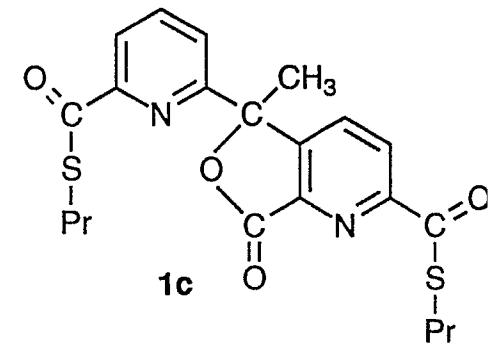
^1H NMR; 300 MHz; CDCl_3 ; 298 K



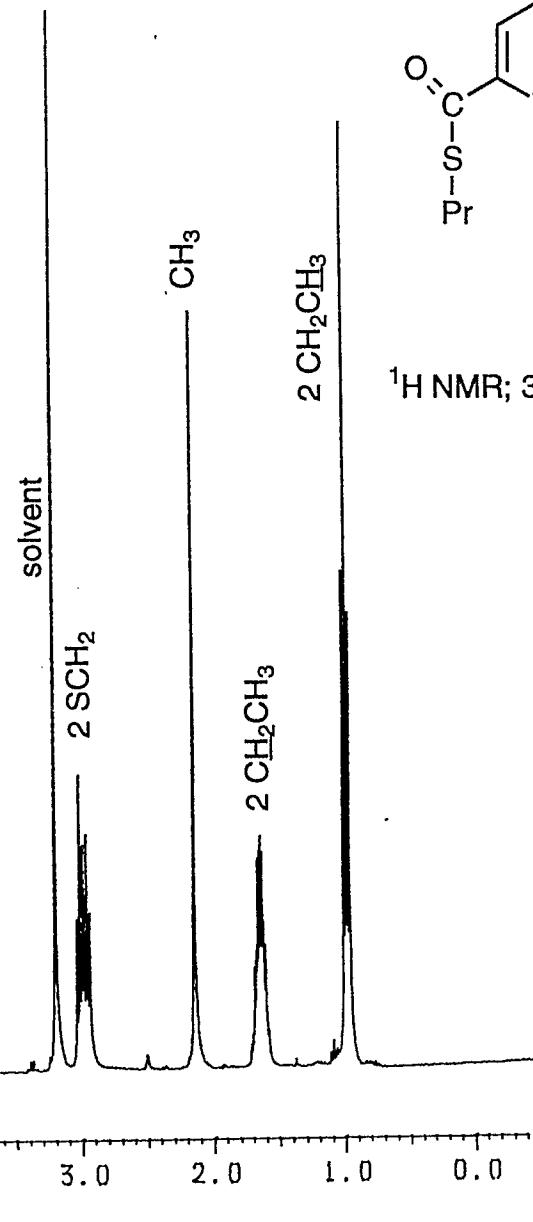


^{13}C NMR; 300 MHz; CDCl_3 ; 298 K

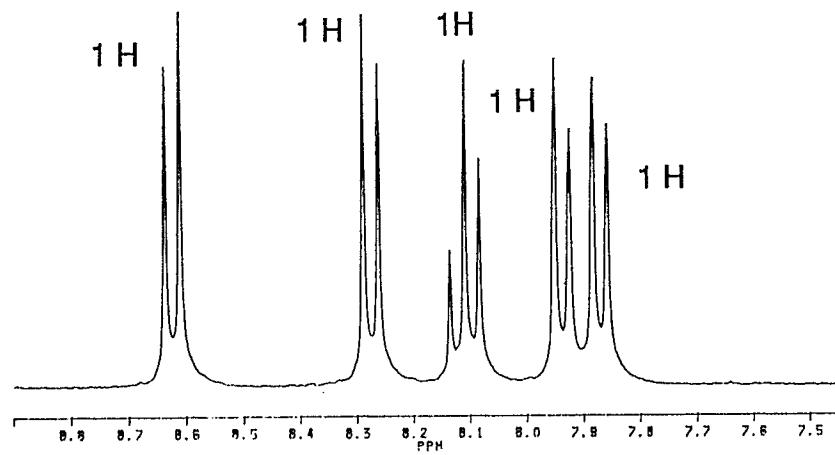




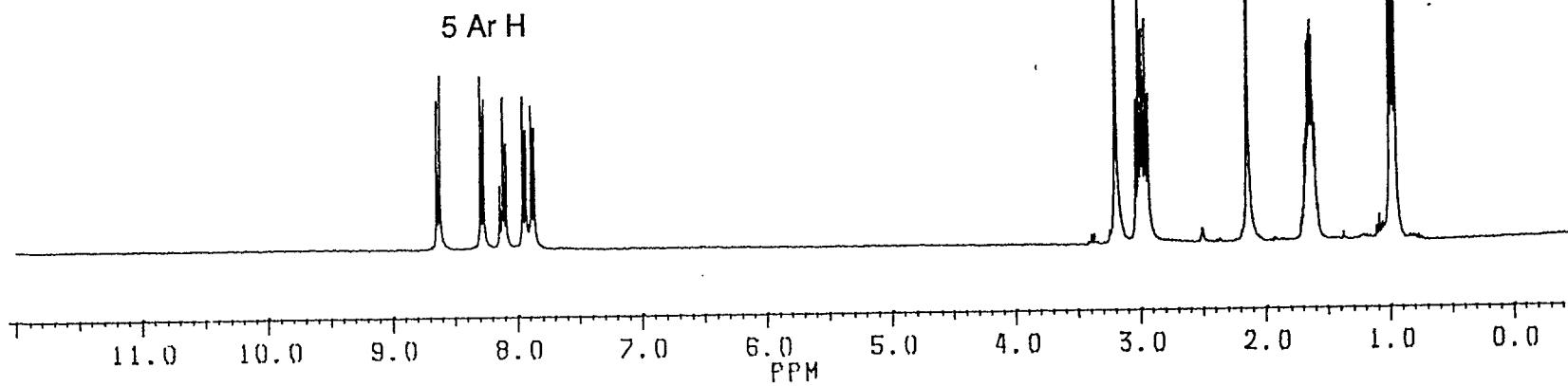
¹H NMR; 300 MHz; (CD₃)₂SO; 313

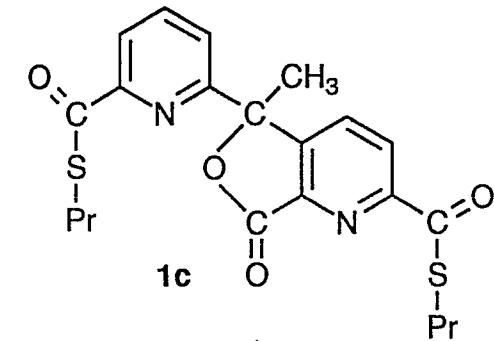
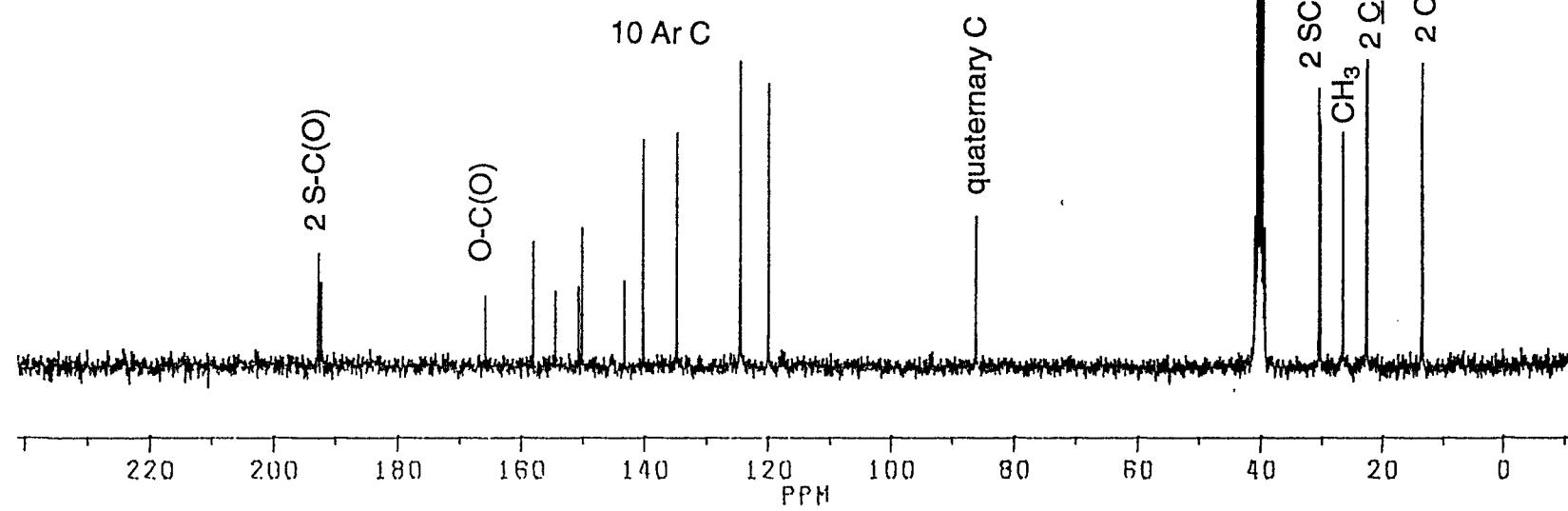
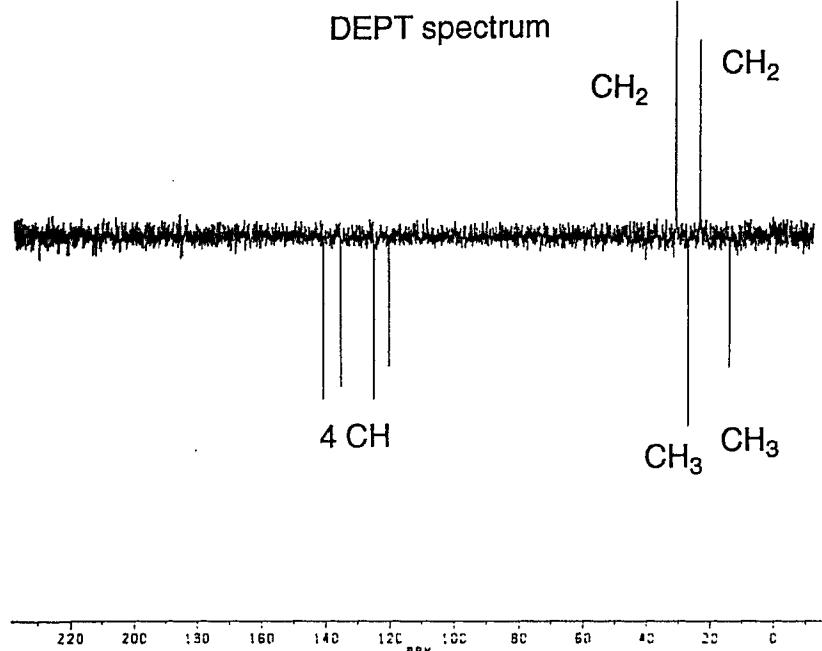


Enlarged aromatic region

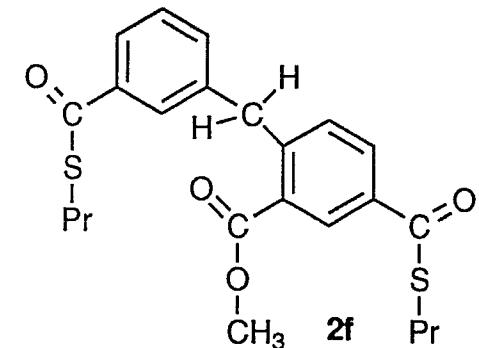
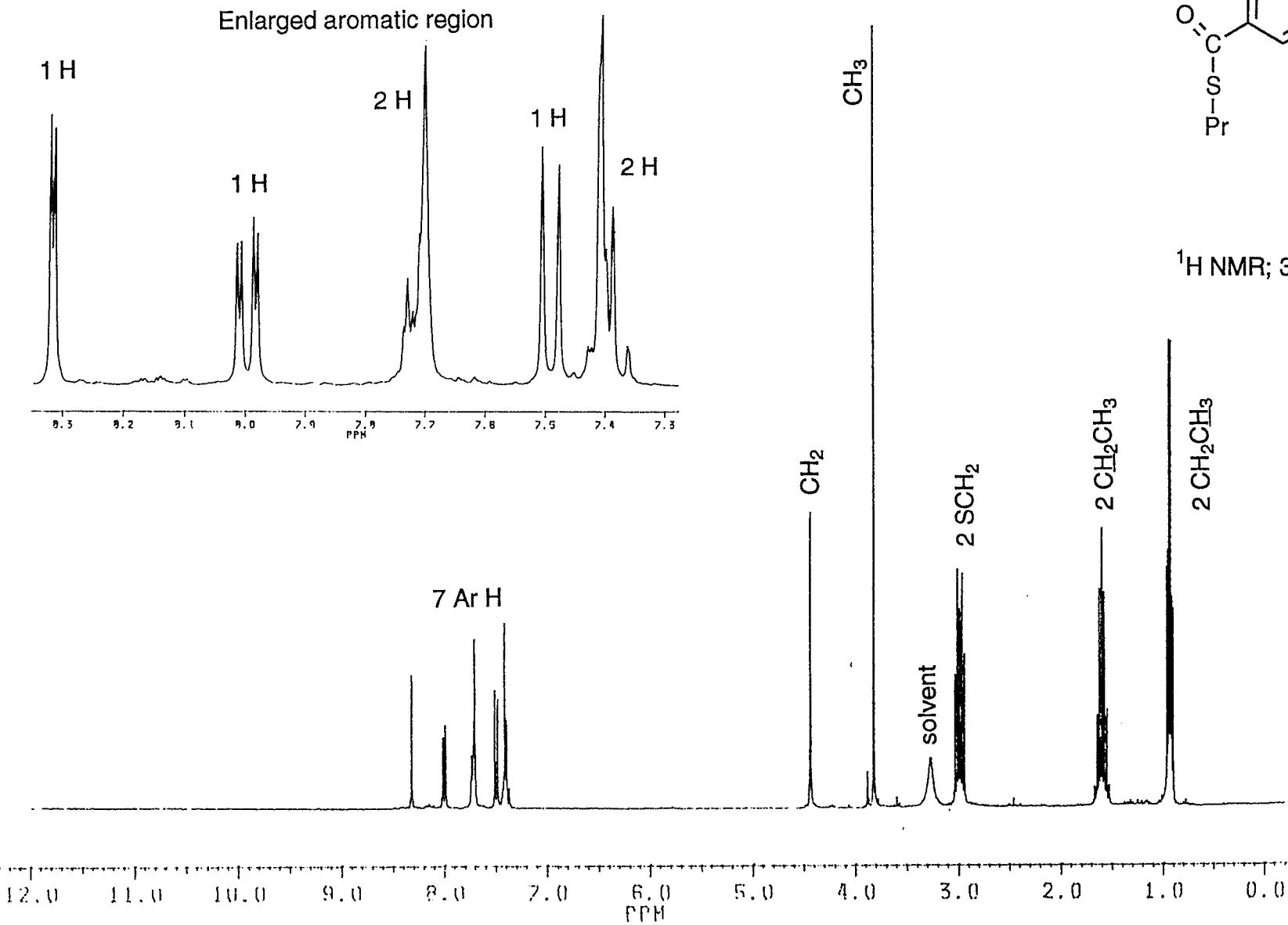


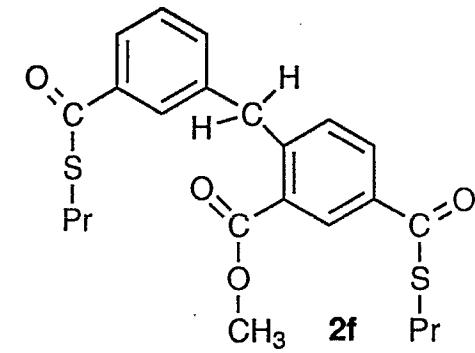
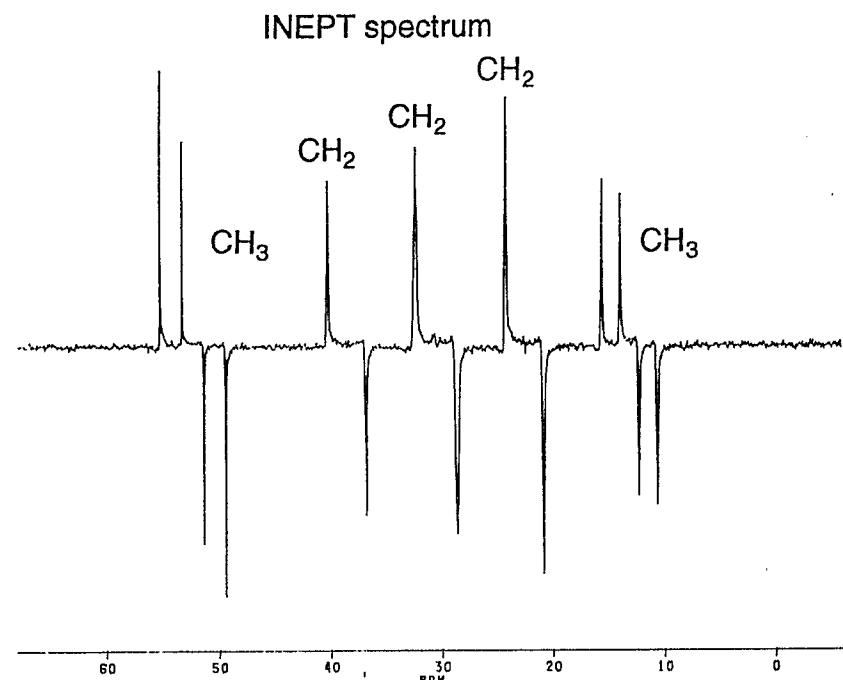
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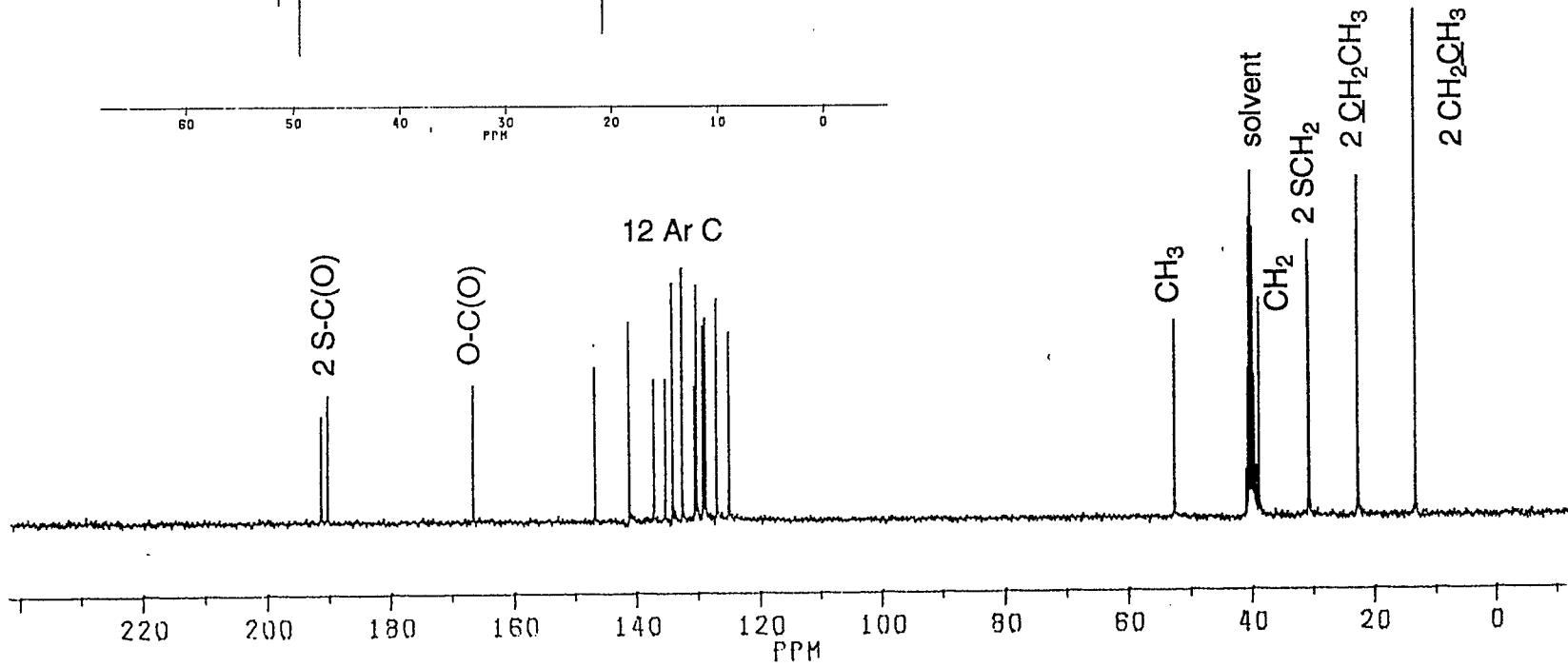


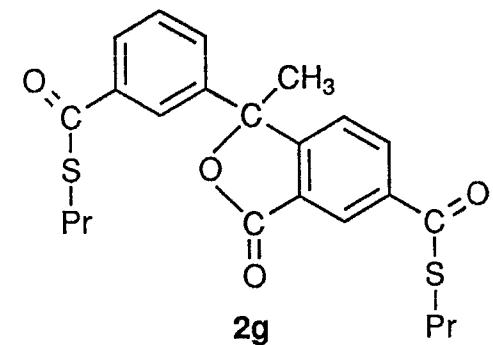
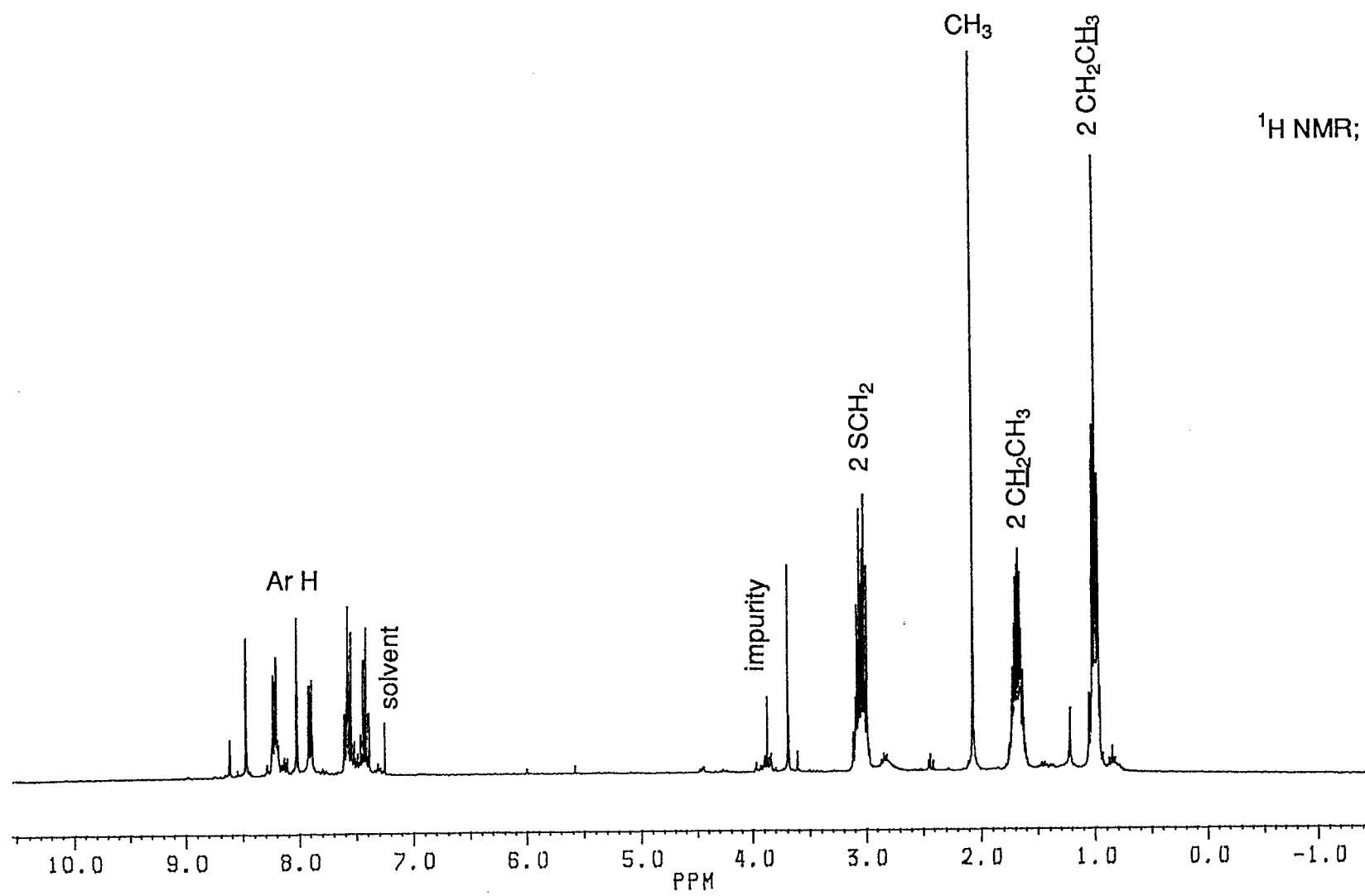
¹³C NMR; 300 MHz; (CD₃)₂SO; 313



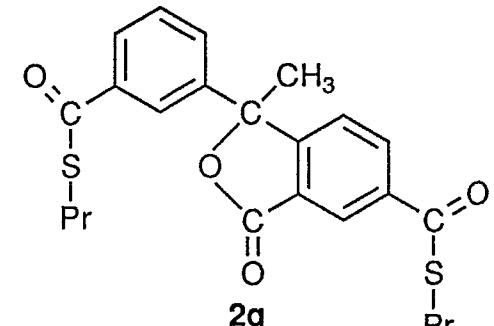
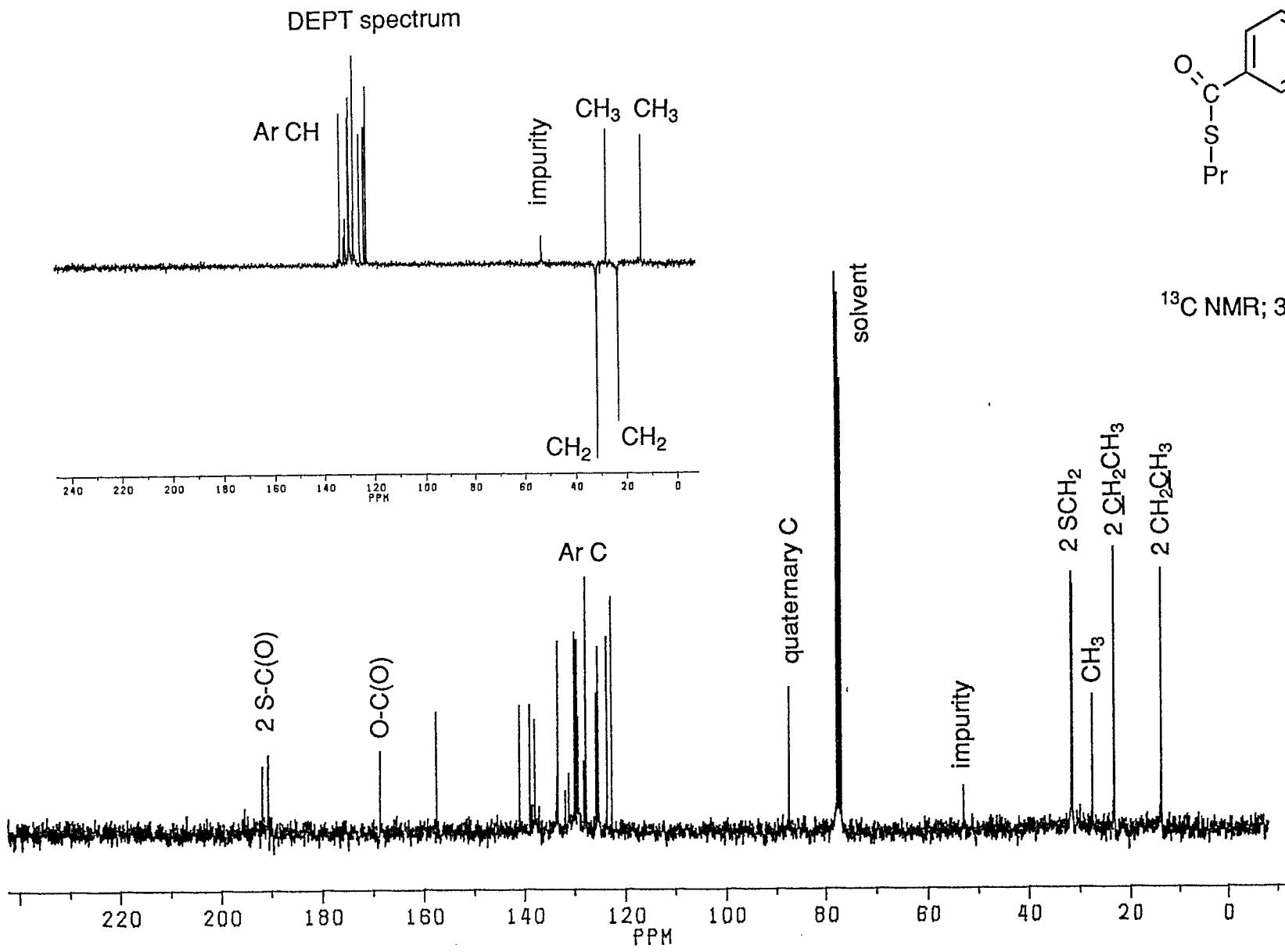


^{13}C NMR; 300 MHz; $(\text{CD}_3)_2\text{SO}$; 313

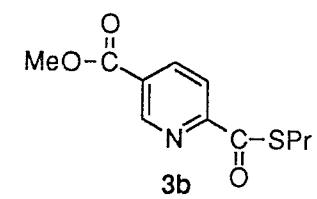




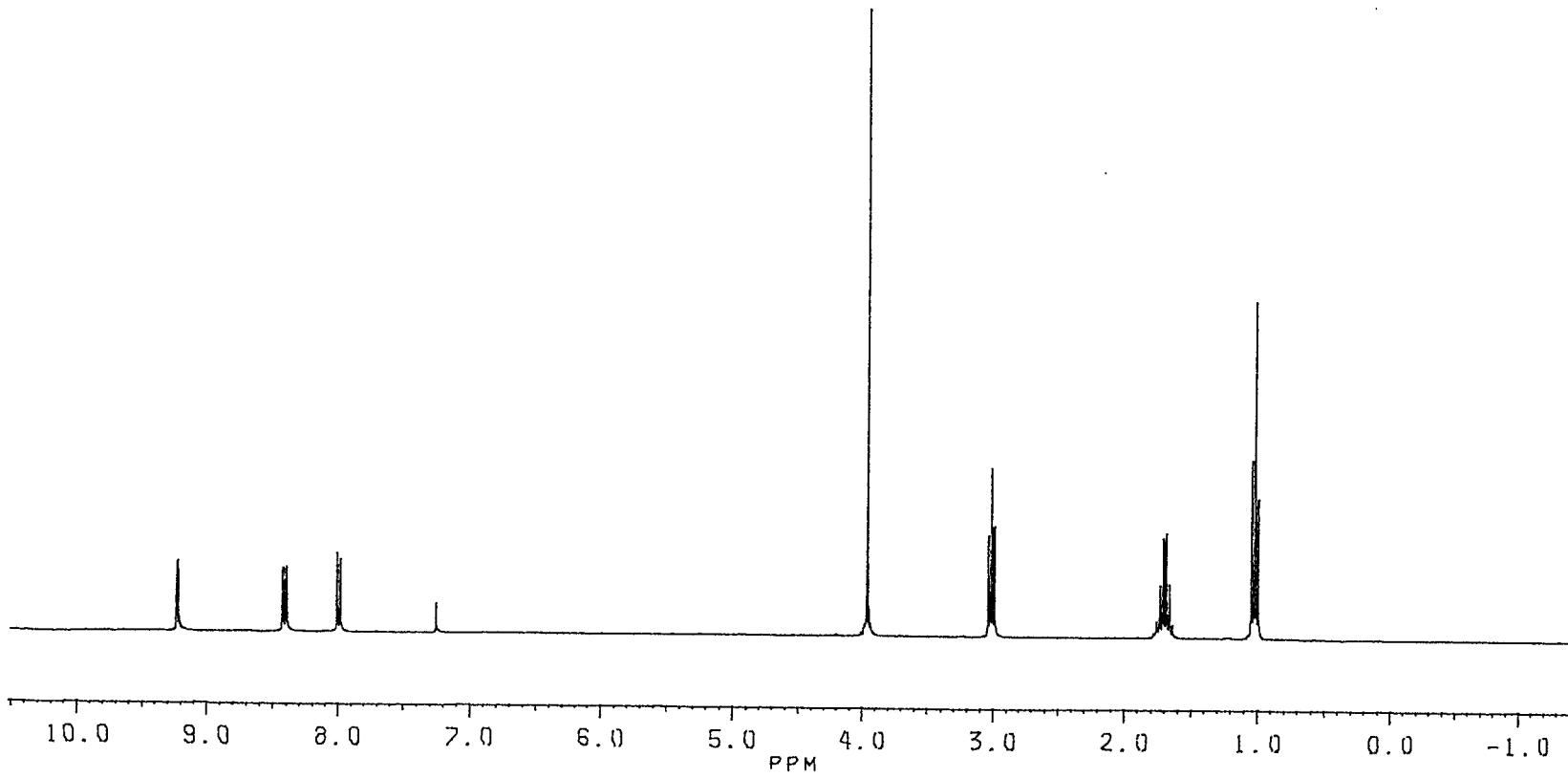
^1H NMR; 300 MHz; CDCl_3 ; 298 K

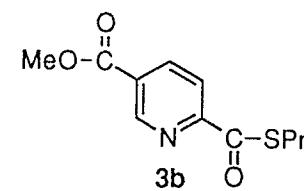


¹³C NMR; 300 MHz; CDCl₃; 298 K

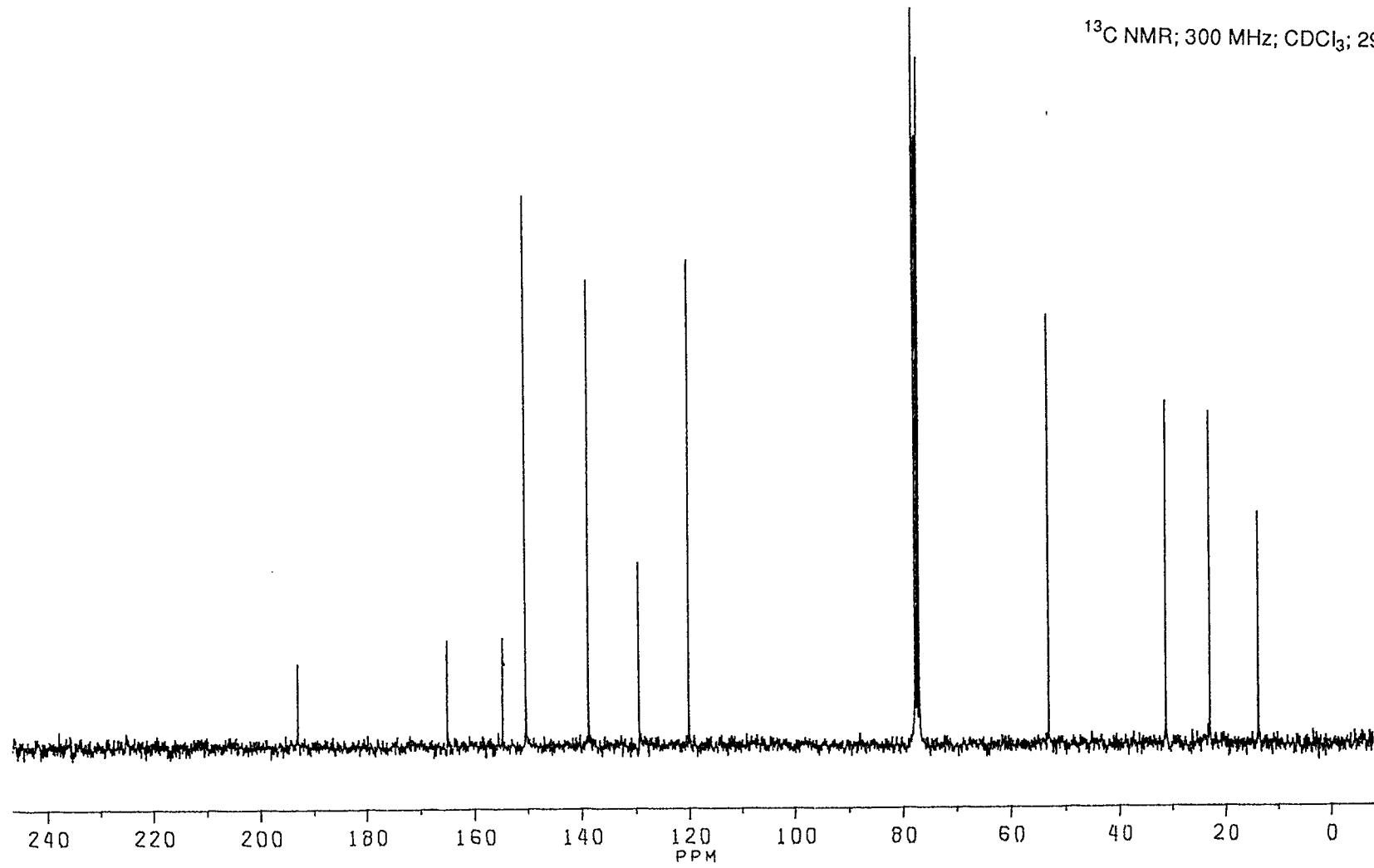


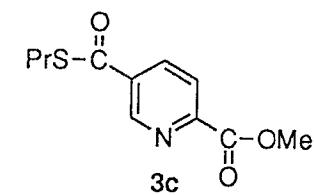
^1H NMR; 300 MHz; CDCl_3 ; 298 K



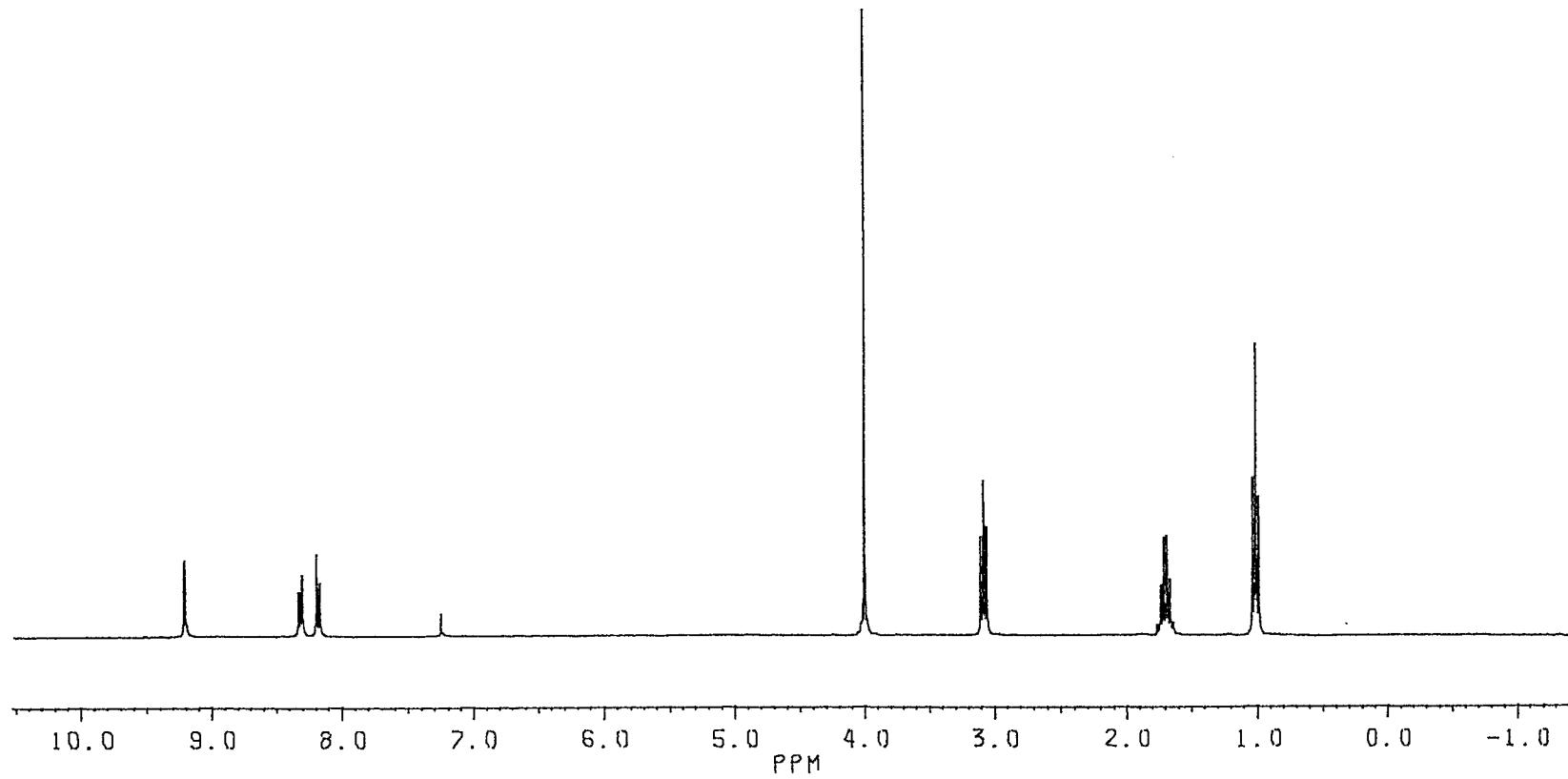


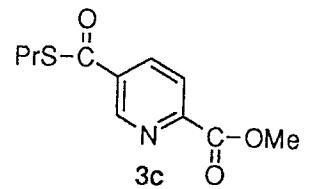
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K



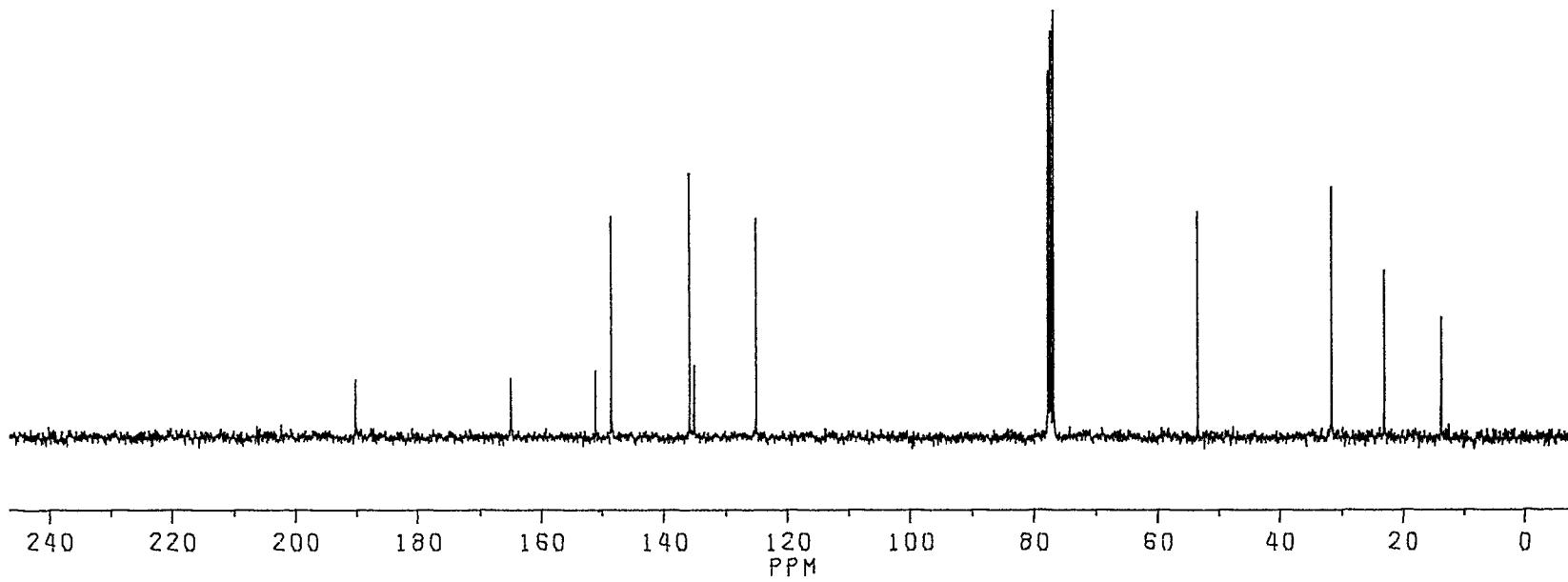


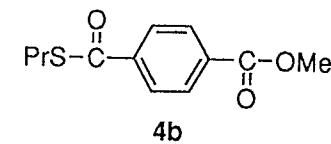
^1H NMR; 300 MHz; CDCl_3 ; 298 K





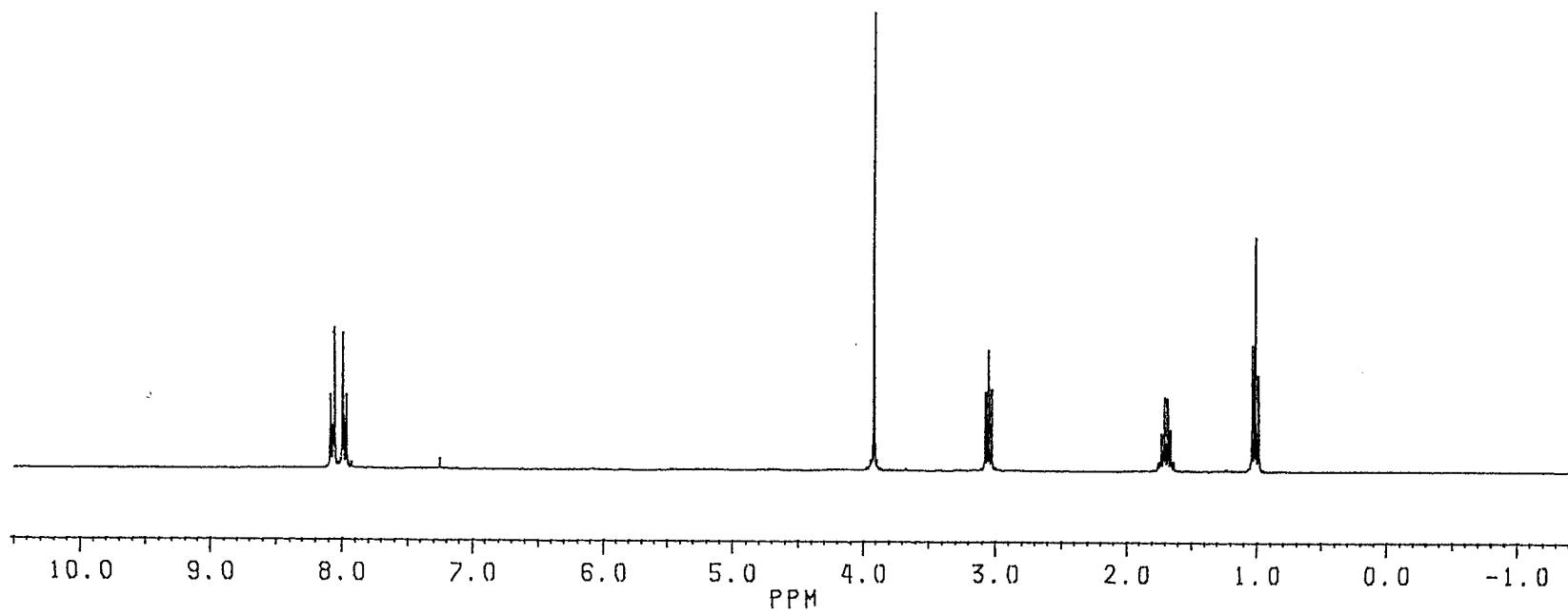
^{13}C NMR; 300 MHz; CDCl_3 ; 298 K

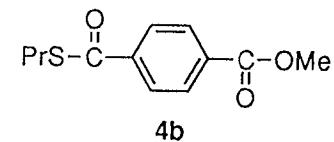




4b

^1H NMR; 300 MHz; CDCl_3 ; 298 K





4b

¹³C NMR; 300 MHz; CDCl₃; 298 K

